THESIS

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Summary.

The thesis is presented in two parts.

Part I. Excess Volumes of Mixing.

In recent years, there have been a number of attempts to form a complete theory of liquid mixtures which would allow the prediction of the thermodynamic properties of a given liquid mixture from a knowledge of the intermolecular forces existing within it. Among the most successful of recent theories have been those by Prigogine and his co-workers of the Brussels school. The latest theory is based upon what is termed the Average Potential model, and permits the prediction of the values of the thermodynamic excess functions of mixing of a given liquid mixture of non-electrolytes from the measured values of such physical properties of the pure, unmixed components as the density, and the heat capacity,

The numerical results obtained from the detailed treatment are in good agreement with experimental measurements on systems of mixtures of molecules of nearly equal size, for example, carbon monoxide and methane.

The theory is, however, not restricted to dealing with systems of mixtures of molecules of similar size and it has been extended to cover the case of mixtures of r-mer molecules. It is this aspect of the Average Potential theory which has been of principal interest in the present work.

One of the most interesting predictions of the theory is that, in mixtures of r-mer molecules, the excess volume of mixing should exhibit minima when the ratio of the chain length of one species in the mixture is approximately an integral multiple of that of the other. It is also possible to calculate theoretical values of the excess volumes and its variation with temperature.

Very little direct experimental evidence has been offered to confirm the validity of the extension of the Average Potential theory to mixtures of r-mer molecules, and it was the intention in the present work to obtain appropriate experimental information which would provide a test of the theory.

The excess volume of mixing of a set of systems of the type cyclohexane + dicyclohexyl, was measured at various temperatures. The choice of systems was such that the moler volume of the second component was approximately twice that of the first component, which was in every case cyclohexane. The second components were all closely related chemically, e.g. dicyclohexyl and dicyclohexylmethane, and thus the variations between systems of the observed excess volume of mixing should depend principally on the differing sizes of the molecules in the systems. It was hoped that the excess volumes of the systems would show a minimum for the system for which the ratio of molar volumes of the components was closest to the integral value, two. The occurrence of such a minimum would provide a direct test of Prigogine's theory. It was also intended to compare the theoretical and experimental values of the excess volume of mixing, v^e, and its variation with temperature, $\frac{dv^e}{dT}$, for each system.

It was found that the agreement between the observed and calculated values of v^e and $\frac{dv^e}{dT}$ was qualitative at best, with regard to magnitude and sign, but the expected minimum in the excess volume was found.

The present research has confirmed that the ideas underlying the extension of the Average Potential theory to mixtures of r-mer molecules is essentially valid, but that the comparison between the observed and calculated values of the excess function is poor.

Part 2. The Preparation and Properties of Aluminium Hydride Etherate.

It has been shown that beryllium hydride, BeH_2, prepared under conditions which produce an ether-free product[†], is less sensitive to moisture and to spontaneous decomposition than the etherate $BeH_2(C_2H_5)_2O$. It was hoped that the same behaviour would be shown by aluminium hydride and its etherate.

Various methods of preparing aluminium hydride in an ether-free condition were investigated. It was found that none of the methods which have been described in the literature, was successful in producing an entirely unetherated product. The aluminium hydride which was obtained did contain less ether than was found in samples obtained by evaporating ethereal solutions to dryness. The reactivity of the former material was greater than that of the latter. This has been ascribed to difference in the molecular structure of the products formed under different experimental conditions.

ERRATA

Page 2: Insert after Equation 1.2.5

"where the subscript n_j means that all n's except n_i remain constant".

Page 5: Equation 1.3.7

For $q = h - v\Delta p$ read $dq = dh - vdp$.

Page 7: Line 12, omit " g^m_{id} and S^m_{id} are both negative", and insert " g^m_{id} is negative and S^m_{id} is positive."

Page 16: After Equation 2.3.4, omit " and ε_{pot} is the potential energy of a molecule" and insert " and ε_{pot} is the potential energy of the whole assembly of N molecules".

Page 16: After Equation 2.3.8, insert "where V^{con} is the configurational volume, S^{con} the configurational entropy, etc."

PART I.

Excess Volumes of Mixing.

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Chapter 1.

The Thermodynamics of Mixtures.

1.1. Introduction.

The basic theory of liquid mixtures requires the use of some of the fundamental principles and relationships of classical thermodynamics. The present chapter consists of an outline of the more important of these but does not include any detailed rigorous derivations.

The nomenclature which will be used follows closely that given in the English translation of "Chemical Thermodynamics" by I. Prigogine and R. Defay.[1] In the sections of the thesis which deal with statistical theories of liquid mixtures, the notation is based on that given in "The Molecular Theory of Solutions" by I. Prigogine.[2]

1.2. Thermodynamic Functions, Relations and Concentration Scales.

The most convenient set of variables which may be used to define completely the state of a condensed phase is the absolute temperature T, the pressure p, and the number of moles n_i, of each component i in the phase. The most useful thermodynamic function which depends directly upon this set of variables is the Gibbs Free Energy G. This function is a thermodynamic potential and thus possesses the useful property that many other thermodynamic functions may be expressed in terms of it, or of its partial derivatives with respect to T, p and n_i.

The Gibbs free energy of a multicomponent system is defined by the following equation,

$$G = U + pV - TS + \sum_i \mu_i n_i \qquad 1.\ 2.\ 1.$$

where U is the internal energy, V is the volume, S is the entropy of the system, and μ_i is the chemical potential of component i. Equation 1.2.1.

may be written as

$$G = H - TS + \sum_i \mu_i n_i \qquad 1.\ 2.\ 2.$$

where H is the enthalpy of the system defined by

$$H = U + pV \qquad 1.\ 2.\ 3.$$

The total differential of G in the independent variables T, p, and n_i is

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \qquad 1.\ 2.\ 4.$$

Thus the partial derivatives of G are

$$\left(\frac{\delta G}{\delta p}\right)_{T,n_i} = V, \quad \left(\frac{\delta G}{\delta T}\right)_{n_i,p} = -S \quad \left(\frac{\delta G}{\delta n_i}\right)_{T,p,n_j} = \mu_i \qquad 1.\ 2.\ 5.$$

The enthalpy is obtained from a combination of 1.2.2. and 1.2.5. and is written in either of the equivalent forms

$$H = G - T\left(\frac{\delta G}{\delta T}\right)_{p,n_i} = -T^2\left(\frac{\delta\left(\frac{G}{T}\right)}{\delta T}\right)_{p,n_i} \qquad 1.\ 2.\ 6.$$

This relationship is known as the Gibbs-Helmholtz equation. A useful function is the heat capacity of the system, at constant pressure, C_p, which is the partial derivative of H with respect to T.

$$C_p = \left(\frac{\delta H}{\delta T}\right)_{p,n_i} \qquad 1.\ 2.\ 7.$$

The quantities of most interest in studies of liquid mixtures are the Gibbs free energy, entropy, enthalpy, volume, chemical potential and heat capacity at constant pressure; it is clear that a knowledge of the Gibbs free energy of a given sysrem as a function of T,p and n_i is sufficient to determine all of the others.

An alternative set of independent variables is (T,V,n_i). The reason for preferring the set (T,p,n_i) is that these may be more easily varied experimentally for condensed phases. The thermodynamic potential which is associated with T,V and n_i is the Helmholtz free energy F. This will be needed in the discussion of statistical thermodynamics; its definition (eqn. 1.2.8.) and a few of its relations which are similar to 1.2.4.-1.2.7. are stated below,

$$F = G - pV \qquad 1.\ 2.\ 8.$$

$$dF = -pdV - SdT + \sum_i \mu_i dn_i \qquad 1.\ 2.\ 9.$$

$$\left(\frac{\delta F}{\delta T}\right)_{V,n_i} = -S, \quad \left(\frac{\delta F}{\delta V}\right)_{T,n_i} = -p, \quad \left(\frac{\delta F}{\delta n_i}\right)_{T,V,n_j} = \mu_i \qquad 1.\ 2.\ 10.$$

$$U = F - T\left(\frac{\delta F}{\delta T}\right)_{V,n_i} = -T^2\left(\frac{\delta\left(\frac{F}{T}\right)}{\delta T}\right)_{V,n_i} \qquad 1.\ 2.\ 11.$$

$$C_V = \left(\frac{\delta V}{\delta T}\right)_{V,n_i} \qquad 1.\ 2.\ 12.$$

where Cv is the heat capacity of the system at constant volume.

The quantities G,F,H,U,S and V are examples of extensive properties since their value depends on the total amount of matter present in the system. It is convenient for many purposes to restrict the total quantity of matter in a given system to one mole of substance. The functions are then known as molar thermodynamic functions and are designated by small letters, for example g is the molar Gibbs free energy, v is the molar volume etc.

When the total quantity of matter in a system is defined as being one mole, the most convenient method of specifying the quantity of each component i in the system is its mole fraction x_i. This is defined by,

$$x_i = \frac{n_i}{\sum_i n_i} \qquad 1.\ 2.\ 13.$$

The molar Gibbs free energy can then be expressed in terms of T,p and x_i instead of T,p and n_i. All the mixtures to be discussed in the present work contain only two components whose mole fractions are related by,

contain only two components whose mole fractions are related by x. 14.

The discussion of polymer solutions often involves the use of values of x_i which are very small and difficult to define experimentally. It is then more convenient to use the volume fraction ϕ_i to define the concentration of component i. This is given by

$$\phi_i = \frac{n_i v_i^\circ}{\sum_i (n_i v_i^\circ)} \qquad 1.\ 2.\ 15.$$

The superscript $^\circ$ denotes a property of a pure component, e.g. v_i° is the molar volume of pure i.

1.3. Thermodynamic Functions of Mixing.

The process of interest in the study of mixtures is the isothermal formation of a multicomponent system of given composition from appropriate quantities of the pure, unmixed components. The thermodynamic behaviour shown by the system is followed by measuring the increase of the various thermodynamic functions on formation of one mole of the mixture. For binary mixtures, the increase in the Gibbs free energy per mole of mixture of composition x_1, x_2 is given by the equation,

$$g^m = g(p,T,x_1) - \left[x_1 g_1^\circ(p,T) + x_2 g_2^\circ(p,T)\right] \qquad 1.\ 3.\ 1.$$

where g is the molar Gibbs free energy of the mixture, g_1° and g_2° are the molar Gibbs free energies of the pure components 1 and 2 respectively, and g^m is the molar Gibbs free energy of mixing. This is defined as the increase in the Gibbs free energy on forming one mole of a mixture of composition x_1 from x_1 moles of component 1 and x_2 moles of component 2 at constant pressure p and temperature T. Similar quantities are defined for enthalpy, entropy, volume and heat capacity at constant pressure. The restrictions about constant temperature and pressure will be omitted in the equations since they apply throughout the discussion.

$$h^m = h - (x_1 h_1^\circ + x_2 h_2^\circ) \qquad 1.\ 3.\ 2.$$

$$s^m = s - (x_1 s_1^\circ + x_2 s_2^\circ) \qquad 1.\ 3.\ 3.$$

$$v^m = v - (x_1 v_1^\circ + x_2 v_2^\circ) \qquad 1.\ 3.\ 4.$$

$$c_p^m = c_p - (x_1 c_{p_1}^\circ + x_2 c_{p_2}^\circ) \qquad 1.\ 3.\ 5.$$

These quantities are all related to g^m using the relations corresponding to equations 1.2.5. to 1.2.7.

$$s^m = -\left(\frac{\delta g^m}{\delta T}\right)_p, \quad v^m = \left(\frac{\delta g^m}{\delta p}\right)_T, \quad h^m = -T^2\left(\frac{\delta\left(\frac{g^m}{T}\right)}{\delta T}\right)_p \qquad 1.\ 3.\ 6.$$

The total quantity of material in the system having been defined as one mole, and the quantity of each component by its mole fraction, it is possible to omit the restriction to constant n_i in the partial derivatives.

The physical significance of two of the mixing functions may be readily shown. The first law of thermodynamics may be written in the form,

$$q = h - v\Delta p \qquad 1.\ 3.\ 7.$$

where q is the heat absorbed by the system during a physico-chemical process. For a process occurring at constant pressure this becomes,

$$dq = dh. \qquad 1.\ 3.\ 8.$$

If the process is one of mixture formation then,

$$dh = h^m = dq \qquad 1.\ 3.\ 9.$$

and h^m is clearly heat absorbed during the formation of one mole of the mixture. This quantity is generally known as the heat of mixing. It should be noted that when h^m is positive, heat is absorbed during the mixing process and when h^m is negative heat is evolved by the system. If the process takes place adiabatically a positive h^m means that the temperature of the mixture decreases.

Similarly, from equation 1.3.4. the volume of mixing, v^m is seen to be the increase in the total volume of the system when one mole of mixture is formed from the pure, unmixed components. When v^E is positive, the ~~unmixed~~ mixture occupies a greater volume than the sum of the volumes of the unmixed components, and when v^m is negative the system displays a contraction on mixing.

1.4. The Thermodynamics of Ideal Mixtures.

The ideal mixture is a hypothetical mixture whose properties are taken as a basis against which the properties of real mixtures are compared. Ideal mixtures may be defined in several closely equivalent ways. The definition adopted here, relates the chemical potential μ_i of component i to its mole fraction x_i,

$$\mu_i^{id}(pTx_i) = \mu_i^{\ominus} + RT\ln x_i \qquad 1.4.1.$$

where $\mu_i^{\ominus}$ is the standard chemical potential of component i and R is the gas constant.

Although most mixtures display ideal behaviour when the concentration of one component is very small, mixtures showing ideal behaviour over the whole composition range are rare. Such mixtures are known as perfect.

The consequences of the definition 1.4.1. may be easily obtained. By integrating equation 1.2.1. at constant temperature and pressure, the following expression for the molar Gibbs free energy of the ideal mixture is obtained,

$$g = x_1\mu_1 + x_2\mu_2 \qquad 1.4.2.$$

The ideal Gibbs free energy of mixing can be found by substituting the values of μ_1^{id} and μ_2^{id} obtained from equn. 1.4.1. into equn. 1.4.2. followed by subtraction of the Gibbs free energies of the pure components,

$$g^m_{id} = \left[\left(x_1\mu_1^\circ + x_1 RT\ln x_1\right) + \left(x_2\mu_2^\circ + x_2 RT\ln x_2\right)\right] - \left[x_1\mu_1^\circ + x_2\mu_2^\circ\right] \qquad 1.\ 4.\ 3.$$

whence,

$$g^m_{id} = RT\left(x_1\ln x_1 + x_2\ln x_2\right) \qquad 1.\ 4.\ 4.$$

The other ideal functions of mixing may be obtained directly from equation 1.4.4.

$$h^m_{id} = -T^2\left(\frac{\delta\left(\frac{g^m_{id}}{T}\right)}{\delta T}\right)_p = 0 \qquad 1.\ 4.\ 5.$$

$$s^m_{id} = -\left(\frac{\delta g^m_{id}}{\delta T}\right)_p = -R\left(x_1\ln x_1 + x_2\ln x_2\right) \qquad 1.\ 4.\ 6.$$

$$v^m_{id} = \left(\frac{\delta g^m_{id}}{\delta p}\right)_T = 0 \qquad 1.\ 4.\ 7.$$

$$C^m_{p\,id} = \left(\frac{\delta h^m_{id}}{\delta T}\right)_p = 0 \qquad 1.\ 4.\ 8.$$

Since x_1 and x_2 are less than unity, it follows from equation 1.4.4. and equation 1.4.6. that g^m_{id} and s^m_{id} are both negative. Consequently, an ideal solution is formed in a spontaneous, irreversible process. Furthermore, since v^m_{id} and h^m_{id} are both zero, the process is unaccompanied by an evolution or absorption of heat or by a change in total volume.

All the relationships derived so far are of complete generality and apply equally to the gaseous, liquid and crystalline phases. The present work is concerned only with mixtures of liquids, which being condensed phases are often termed solutions, and therefore it is necessary to investigate the additional conditions which this restriction involves.

Since a liquid mixture may exist at a temperature above the critical temperature of one of its components, the standard chemical potential $\mu_i^\ominus$ may refer to a physically unrealiseable state. Also since the vapour pressure of a liquid mixture usually is less than that of one of its components at a given temperature, the value of $\mu_i^{\ominus}$ can refer to a pure liquid existing under a pressure less than its vapour pressure at the given temperature. This is again physically unrealiseable. Fortunately $\mu_i^{\ominus}$ changes only slowly with pressure at temperatures well below the critical temperature and thus both inexactnesses in the definition 1.4.1., as applied to liquid mixtures, vanish when its use is confined to low pressures and to temperatures well below the critical temperature.

Secondly, since the definitions of the mixing functions of ideal solutions are all derived from the definition of the ideal solution given by equation 1.4.1., it follows that for a solution to display ideal behaviour all of these relationships must be obeyed. For example the fact that a given mixture of liquids is formed without heat or volume change does not necessarily confirm ideality.

The definition of an ideal solution employed in this discussion may be briefly compared with another commonly used definition of an ideal solution as one which obeys Raoult's law. This may be written in the form,

$$p = x_1 p_1^{\circ} + x_2 p_2^{\circ} \qquad 1.\ 4.\ 9.$$

where the p is the total vapour pressure of the mixture and p_1° and p_2° are the vapour pressures of the pure unmixed components. This expression can be obtained from the definition 1.4.1. only after making the following assumptions. The molar volume of the liquid phase is taken to be negligibly small compared to that of the vapour phase, and the vapour is assumed to obey the perfect gas law.

$$pV = RT \qquad 1.\ 4.\ 10.$$

Although the first assumption is a reasonable one under many conditions, even at low pressures most gases and vapours deviate markedly from perfect gas behaviour. The definition 1.4.1. is free from these assumptions and is thus preferred as a basis for the treatment of ideal solutions.

1.5. The Thermodynamics of Non-Ideal Mixtures.

Most real mixtures do not display ideal behaviour. It has become customary to represent the departures from ideality of non-ideal solutions in one of two fashions. The first method, using activity coefficients, was introduced by G.N. Lewis.[3] The chemical potential of component i in a non-ideal mixture is defined as

$$\mu_i (T p\, x_i) = \mu_i^{\ominus} (T p) + RT \ln \gamma_i x_i \qquad 1.\ 5.\ 1.$$

where γ_i is the activity coefficient of component i. The product $x_i \gamma_i$ is known as the absolute activity of component i. It is clear that the values of the activity coefficients describe the extent of the non-ideality of the mixture.

The thermodynamic functions of mixing of a real mixture can be obtained in terms of the activity coefficients using equation 1.5.1. The expressions obtained are the following,

$$g^m = RT \left(x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2 \right) \qquad 1.\ 5.\ 2.$$

$$h^m = -RT^2 \left(x_1 \frac{\delta \ln \gamma_1}{\delta T} + x_2 \frac{\delta \ln \gamma_2}{\delta T} \right) \qquad 1.\ 5.\ 3.$$

$$s^m = -R \left(x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2 \right) - RT \left(x_1 \frac{\delta \ln \gamma_1}{\delta T} + x_2 \frac{\delta \ln \gamma_2}{\delta T} \right) \qquad 1.\ 5.\ 4.$$

$$v^m = +RT \left(x_1 \frac{\delta \ln \gamma_1}{\delta p} + x_2 \frac{\delta \ln \gamma_2}{\delta p} \right) \qquad 1.\ 5.\ 5.$$

$$C_p^m = \frac{\delta h^m}{\delta T} \qquad 1.\ 5.\ 6.$$

The use of activity coefficients is convenient when the non-ideality of one component in a solution is being examined or when the predictions of a refined theory of solutions are being compared with experimental quantities.

When a general picture of the non-ideality of the whole solution is saught, it is more common to use the excess thermodynamic functions of mixing which were introduced by G. Scatchard.[4]

An excess thermodynamic function X^e is defined as the excess of the value of the thermodynamic function of mixing of a real solution X^m over that of an ideal mixture of the same composition, formed at the same temperature X^m_{id}. The superscript ^{e} denotes an excess function, for example the molar excess Gibbs free energy of mixing is given by

$$g^e = g^m - g^m_{id} \qquad 1.\ 5.\ 7.$$

The excess functions are closely related to the activity coefficients,

$$g^e = RT\left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right) \qquad 1.\ 5.\ 8.$$

$$h^e = -RT^2\left(x_1 \frac{\delta \ln \gamma_1}{\delta T} + x_2 \frac{\delta \ln \gamma_2}{\delta T}\right) \qquad 1.\ 5.\ 9.$$

$$s^e = -R\left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right) - RT\left(x_1 \frac{\delta \ln \gamma_1}{\delta T} + x_2 \frac{\delta \ln \gamma_2}{\delta T}\right) \qquad 1.\ 5.\ 10.$$

$$v^e = +RT\left(x_1 \frac{\delta \ln \gamma_1}{\delta p} + x_2 \frac{\delta \ln \gamma_2}{\delta p}\right) \qquad 1.\ .\ 11.$$

$$C_p^e = \left(\frac{\delta h^e}{\delta T}\right) \qquad 1.\ 5.\ 12.$$

The molar excess Helmholtz free energy of mixing, f^e, may be defined by

$$f^e = g^e - pv^e \qquad 1.\ 5.\ 13.$$

When dealing with liquid mixtures of non-electrolytes at room temperatures, typical values of g^e and v^e are 20cal.mole^{-1} and 0.2cm^3.mole^{-1}. In this case the difference between g^e and f^e is 0.005cal.mole^{-1} and may be neglected. Similarly u^e and h^e may be taken as equal.

Since the enthalpy and volume of mixing of an ideal solution are zero it follows that

$$h^e = h^m \qquad 1.\ 5.\ 14.$$

$$v^e = v^m \qquad 1.\ 5.\ 15.$$

These results are of importance in the experimental determination of the excess functions.

1.6. Experimental Determination of Excess Functions.

The excess Gibbs free energy of mixing may be obtained from measurements of the activity coefficients of the components of a mixture using equation 1.5.8. This is most commonly carried out by measuring the pressure and composition of the vapour in equilibrium with a solution of known composition at a fixed temperature.[5] Provided that sufficient information is available to make accurate correction for gas imperfection, it is then a simple matter to evaluate g^e. Unfortunately the information required includes the second virial coefficients, both of the pure components and of the mixture. These are frequently known only imprecisely and the derived excess functions are of limited accuracy.

In certain cases, when one component is much less volatile than the other (e.g. benzene-diphenyl[6,7]) it is sufficient to measure the total pressure of the solution and its composition, from these the activity coefficient of the more volatile component may be calculated. The activity coefficient of the second component is obtained using the Gibbs-Duhem equation and g^e is then found using equation 1.5.8. It should be noted that the value of g^e obtained by this method contains errors introduced in the integration required by the application of the Gibbs-Duhem equation.

In the last section it was shown that the excess enthalpy of mixing is equal to the heat of mixing at constant pressure per mole of solution, thus suggesting that the most direct means of determining h^e would be a calorimetric method. This is found to be the case in practice,[8] although care is required to eliminate errors due to evaporation which can be large compared with the small heat of mixing.

Alternatively, h^e may be obtained from measurements of g over a range of temperature followed by a calculation based upon the Gibbs-Helmholtz equation. The value of this method is diminished by the relatively limited range of temperature over which g^e can usually be conveniently measured. This leads to an inaccuracy in the derived values of h^e which is frequently one order of magnitude greater than the inaccuracy of the original values of g^e. A further drawback to the method is that h^e is assumed to be temperature independent which is not always true as is shown by the non-zero values of c_p^e. The calorimetric method of determining h^e is more satisfactory and is always to be preferred.

The excess entropy of mixing, s^e, is almost always found from the relation,

$$s^e = \frac{h^e - g^e}{T} \qquad 1.\ 6.\ 1.$$

If h^e is obtained from values of g^e, then the derived value of s^e suffers from the same imprecision as h^e.

The excess volume of mixing, v^e, is obtained from measurements of the volume change which takes place when a solution is formed from its components. Methods of determining this will be discussed in a later section.

The excess heat capacity is normally measured calorimetrically.[9] An alternative method requiring the determination of the isentropic thermal pressure coefficient $\left(\frac{\delta T}{\delta P}\right)_S$ and the coefficient of thermal expansion $\left(\frac{\delta V}{\delta T}\right)_P$ of the given mixture has been described.[10] The heat capacity of the system is calculated from the equation,

$$C_P = T\left(\frac{\delta V}{\delta T}\right)_P \div \left(\frac{\delta T}{\delta P}\right)_S \qquad 1.\ 6.\ 2.$$

This method offers little advantage compared with the straightforward calorimetric method.

Chapter 2.

The Statistical Thermodynamics of Solutions.

2.1. Introduction.

The object of this chapter is to present a brief outline of the methods whereby statistical thermodynamics is used to inter-relate the bulk properties of matter, particularly of binary liquid mixtures, with the properties of the molecules of which matter is composed. The molecular property of principal interest in theories of liquid mixtures is the energy of interaction between molecules; closely related to this is the configurational partition function and an explanation is given of the importance of this quantity in most current theories of liquid mixtures.

2.2. The Partition Function.

One of the fundamental equations of statistical mechanics is the relationship between the Helmholtz free energy F and the partition function Z of a given system. The relationship is

$$F = -kT \ln Z \qquad 2.\ 2.\ 1.$$

where k is the Boltzmann constant. The partition function Z is a function of molecular properties, especially of the energy levels of molecules. It may be defined in two equivalent forms. The first definition, known as the quantum partition function, is used when the separation between the possible energy levels for a molecule is relatively large. The definition is

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}} \qquad 2.\ 2.\ 2.$$

ε_j is the energy of a given quantum state j. The classical partition function which is employed when the quantum states are separated by vanishingly small energy differences, is given by

$$Z = \frac{1}{h^N} \int \cdots \int e^{-\frac{\varepsilon}{kT}} d\tau_1 \ldots d\tau_N \, dp_1 \cdots dp_N \qquad 2.\ 2.\ 3.$$

In this expression h is Planck's constant, N is the number of molecules in the system, r_N is the positive vector specifying the position of the N^{th} molecule and p_N is the corresponding momentum vector. The integrations are carried out between the limits $+\infty$ and $-\infty$ for p_N and between limits defining the volume of the system for v_N.

It can be seen that Z, however it is defined, is a property of the molecules of a given system. Equation 2.2.1. relates experimentally observable thermodynamic properties of bulk matter to properties of molecules through the partition function.

The other thermodynamic functions are obtained using the following expressions,

$$U = kT^2\left(\frac{\delta \ln Z}{\delta T}\right)_V \qquad 2.\ 2.\ 4.$$

$$S = k \ln Z + kT\left(\frac{\delta \ln Z}{\delta T}\right)_V \qquad 2.\ 2.\ 5.$$

$$p = kT\left(\frac{\delta \ln Z}{\delta V}\right)_T \qquad 2.\ 2.\ 6.$$

$$C_V = \left(\frac{\delta}{\delta T}\left(kT^2 \frac{\delta \ln Z}{\delta T}\right)_V\right)_V \qquad 2.\ 2.\ 7.$$

2.3. <u>The Factorisation Property of the Partition Function.</u>

The form of the partition function given by 2.2.2. shows that if the energy ε_j of a given quantum state j may be taken as the sum of contributions ε'_j, ε''_j, ε'''_j, etc., that is if

$$\varepsilon_j = \varepsilon'_j + \varepsilon''_j + \varepsilon'''_j + \ldots\ldots \qquad 2.\ 3.\ 1.$$

then the partition function may be written as a product of factors.

$$Z = \left(\sum e^{-\frac{\varepsilon'_j}{kT}}\right) \times \left(\sum e^{-\frac{\varepsilon''_j}{kT}}\right) \times \ldots\ldots \qquad 2.\ 3.\ 2.$$

Much use is made of this factorisation property since the total energy of a molecule can generally be taken as being made up of independent separable contributions from different degrees of freedom such as vibrational, rotational, etc. This separation is an approximation but is generally valid. The partition function of a system of molecules can then be written as the product of a number of factors each related to different degrees of freedom.

A convenient division for the present purpose is to consider the contributions from the external and internal degrees of freedom of a molecule as separable. The total partition function Z may then be written as

$$Z = Z_{int.} \times Z_{ext.} \qquad 2.\ 3.\ 3.$$

where Z_{int} is the partition function for the internal degrees of freedom of a molecule such as the rotational, vibrational and electronic degrees of freedom. The partition function for external degrees of freedom $Z_{ext.}$, may be factorised further on the basis of the separation of the contribution from the kinetic and potential energies of the molecules. The external partition function may be then written as

$$Z_{ext.} = Z_k \times Q \qquad 2.\ 3.\ 4.$$

where Z_k is the kinetic partition function and Q is the configurational partition function. It is found that Z_k is a function only of the absolute temperature T.

The value of the configurational partition function in theories of liquid mixtures is that even the most sophisticated theories yet developed assume that the mixing process affects Q only. This assumption implies that the internal degrees of freedom are independent of a changing environment. Clearly the thermodynamic functions of mixing are functions of Q alone. The classical definition of the configurational partition function may be written as

$$Q = \frac{1}{N!}\int \cdots\cdots \int e^{\left(-\frac{\mathcal{E}_{pot}}{kT}\right)} d\tau_1 \cdots\cdots d\tau_N$$ 2. 3. 5.

where the limits of integration are the same as before, and $\mathcal{E}_{pot}$ is the potential energy of a config^{n} molecule.

The thermodynamic functions related to Q are the configurational thermodynamic functions which are given by

$$V^{con} = kT^2\left(\frac{\delta \ln Q}{\delta T}\right)_V$$ 2. 3. 6.

$$S^{con} = k \ln Q + kT\left(\frac{\delta \ln Q}{\delta T}\right)_V$$ 2. 3. 7.

$$C_V^{con} = \left(\frac{\delta}{\delta T} kT^2\left(\frac{\delta \ln Q}{\delta T}\right)_V\right)_V$$ 2. 3. 8.

Of particular interest in the present work is the relationship between Q and the pressure of the system p. This is obtained by combining equations 1.2.10. with the fact that Z depends on V only through Q.

$$p = kT\left(\frac{\delta \ln Q}{\delta V}\right)_T$$ 2. 3. 9.

This relationship contains apart from Q, a relationship between p, V and T. It is thus an equation of state related directly to molecular properties through Q. This equation forms the basis of the method whereby the excess volume of mixing of a binary liquid system is calculated from the properties of the molecules of the system.

It has been shown that the mixing process affects the configurational part of the partition function only, and therefore the thermodynamic functions of mixing are determined by changes in the configurational partition function. As a consequence of this, theories of solutions are essentially concerned with the evaluation of the configurational partition function.

The definition of Q given by 2.3.5. may be extended to mixtures of components 1 and 2 for which the configurational partition function is given by

$$Q = \frac{1}{N_1!\,N_2!}\int \cdots \int e^{\left(-\frac{\epsilon_{all}}{kT}\right)} (dr_1)^{N_1} (dr_2)^{N_2} \qquad 2.\ 3.\ 10.$$

2.4. The Molecular Distribution Function.

An alternative approach to theories of mixtures lies in the use of the molecular distribution functions which define the probability of obtaining particular arrangements of molecules in a given system. The detailed treatment[4] involves the solution of a set of integro- differential equations for which a number of simplifying approximations must be made. In spite of the use of these, the method has furnished few numerical results for pure liquids and fewer for mixtures of liquids.

For this reason, and on account of the lack of a treatment based upon molecular distribution of the type of polymer solution which is discussed in this work, no further reference will be made to this method.

Chapter 3.

Intermolecular Forces and Theories of Solutions.

3.1. Introduction.

In the last chapter it was shown that the essential problem in theories of solutions is the evaluation of the configurational partition function. The intention in this chapter is to present a brief discussion of the properties of intermolecular forces which are required for this evaluation, followed by an indication of how it has been carried out in some recent theories. In particular, the treatment of liquid mixtures developed by I. Prigogine and the Brussels school will be discussed, and out of this discussion the reasons for the present research will be presented.

3.2. Intermolecular Forces.

The configurational partition function requires for its evaluation, a knowledge of the potential energy between the molecules as a function of their position and orientation. Information on this subject[12,13] has been obtained from two sources. Firstly, calculations based upon quantum mechanics and classical electrostatics and secondly, experimental measurements of certain of the macroscopic properties of matter which can be directly related to the intermolecular potential energy.

The present state of knowledge concerning intermolecular forces is such that reliability can be placed only on those theoretical calculations which refer to interactions between atoms of low atomic number and between very simple molecules. The results however can be expected to provide a good guide to the behaviour of more complex molecules, provided that they are non-polar and quasi-spherical.

The properties of matter which have provided most information on intermolecular forces fall into three groups.

1. The thermodynamic properties of dilute gases, of which the most useful are the second virial coefficient and the Joule-Thomson coefficient.
2. The transport properties of dilute gases in particular, the viscosity, the diffusion, the thermal diffusion and the thermal conductivity.
3. The thermodynamic properties of crystals at low temperatures including the compressibility, the latent heat of sublimination, the equation of state and the crystal structure.

The mathematical formulation of the intermolecular potential between similar molecules usually depends upon two assumptions. Firstly, the total potential energy of the assembly of molecules is assumed to be the sum of the energies of interaction between all possible pairs of molecules in the assembly. This is generally a valid assumption when the degree of order in the system is low, as in a liquid. Secondly, it is assumed that the expression for the energy of interaction between any pair of molecules, the pair potential, can be written as the sum of two terms, one referring to attraction between the molecules and the other to mutual repulsion. This assumption is suggested by the need for allowing for the intermolecular attraction which causes gases to condense and liquids to freeze, and for the repulsion which is responsible for the low compressibility of crystals and their finite volume near the absolute zero of temperature. In accordance with the normal convention of mechanics, the attractive part of the potential is given a negative sign and the repulsive part is given a positive sign.

The most widely used potential is the bi-reciprocal Lennard-Jones potential,

$$\varepsilon(r) = -Ar^{-m} + Br^{-n} \qquad 3.2.1.$$

where $\varepsilon(r)$ is the intermolecular energy as a function of the distance of separation r, A and B are the coefficients of the attraction and repulsion terms respectively and n and m are indices. The values of A and B are characteristic of the interacting species and are temperature independent.

The attraction between non-polar molecules has been shown by London to be due to dispersion forces.[14] These arise from the attraction between the in-phase oscillations of the electronic systems of adjacent molecules and give rise, in the first approximation, to a term containing r^{-6} .[4]

The repulsion between molecules is due to the interaction between the closed electron clouds of the molecules. According to the calculations of quantum mechanics, this should be described by a term of the form $P(r)\exp(-br)$ where $P(r)$ is a polynomial in r, and b is a positive parameter.[15] This unwieldy expression is frequently simplified to the exponential term only, and for many purposes a further simplification to an inverse power term of the form r^{-n} is employed as in the Lennard-Jones potential. It has been shown that the value of n is not critical provided that it lies between 9 and 14.[16] The mathematical convenience of n = 12 is great and this value is generally chosen. The reason for the unimportance of the precise value of n in theories of liquids is that ordinary liquids are sufficiently expanded to minimise the effects of the approximation in the repulsive term.

The Lennard-Jones potential may be written in a particular form using the values n = 12, m = 6 indicated by the fore-going discussion.

$$\varepsilon(r) = \varepsilon^{*}\left[\left(\frac{r^{*}}{r}\right)^{12} - 2\left(\frac{r^{*}}{r}\right)^{6}\right] \qquad 3.\ 2.\ 2.$$

The expression contains two parameters ε^{*} and r^{*} which are determined by the nature of the interacting species; r^{*} is the equilibrium separation of the species and ε^{*} is the energy corresponding to this separation. This form of the Lennard-Jones potential is known as the Lennard-Jones (12 - 6) potential and although it is not the only potential which gives an explicit form for $\phi(r)$,[12] it is one of the simplest and is adequate for many purposes. Among the evidence in its favour is the following.[17]

1. It reproduces the temperature variation of the second virial coefficient of the inert gases over a fairly wide range of temperature.

2. It reproduces the viscosity, thermal conductivity and coefficient of self-diffusion of the inert gases using the same values of ε^* and r^*, which are used to fit the second virial coefficient.

3. It reproduces the latent heat of sublimation, lattice spacing and coefficient of thermal expansion of crystalline argon at low temperatures, using nearly the same values of ε^* and r^* as in 1. and 2.

The Lennard-Jones (12 - 6) potential is not so successful in the calculation of the more sensitive macroscopic properties of pure substances such as the third virial coefficient and the coefficient of thermal diffusion, but for the present work it is quite satisfactory. The reason for its suitability in theories of liquid mixtures are set out below.

1. It is probable that shortcomings in liquid mixture theory are due mainly to the essentially naive structural models used, and to a lesser extent to the statistical treatment of these models rather than defects in the chosen pair potential.

2. The Lennard-Jones (12 - 6) potential is mathematically uncomplicated compared to many other pair potentials and it contains only two variable parameters. It will be found in the next section that this is a requirement of the principle of corresponding states upon which theories of liquid

mixtures depend. Many of the more complicated pair potentials lack this useful property.

The multiatomic globular types of molecule, such as cyclohexane, which form the subject of the present investigation do not completely satisfy the requirements of the Lennard-Jones potential which should be expected to apply strictly only to small molecules and the inert gases.[18] The interactions between globular molecules do not have the geometrical centres of the molecules as origins, but rather are centred upon the peripheral atoms of the molecule. This change of origin affects the interaction in a number of ways and various modifications of the Lennard-Jones (12 - 6) potential have been suggested to take account of them.

The most notable of these are the approach of Kihara,[19] who replaced the point of interaction centres by "cores of interaction", and that of Hamann and Lambert,[20] who found that the thermodynamic properties of globular molecules were better represented by a Lennard-Jones (28 - 7)potential.

In the present work only a (12 - 6) potential is employed, largely because it has been used in the detailed treatment of most current theories of liquid mixtures. It would be interesting to compare the theoretical, numerical results of these treatments with results based upon a (28 - 7) potential.

The theoretical treatment of interactions between unlike molecules rests on a much less secure foundation than that of like molecule interactions. Formally, for pairs of unlike spherical, non-polar molecules, the interaction may be represented by an equation of the Lennard-Jones type with parameters ϵ_{12}^* and r_{12}^* which are determined among other things by the nature of the interacting molecules. The most obvious approach is to relate the interaction parameters for the unlike pair to the interaction parameters ε^*_{11}, ε^*_{22}, r^*_{11}, r^*_{22} for the pure components 1 and 2.

A common relationship which holds for spherical, non-polar molecules usually within about ± 2 % is the following.[21,22]

$$\varepsilon^*_{12} = (\varepsilon^*_{11}\ \varepsilon^*_{22})^{\frac{1}{2}} \qquad 3.\ 2.\ 3.$$

$$r^*_{12} = \tfrac{1}{2}(r^*_{11} + r^*_{22} \qquad 3.\ 2.\ 4.$$

The justification for these rules is largely empirical although there is some theoretical justification for 3.2.3. This is obtained from the London theory of dispersion forces which indicates that the attraction between a pair of unlike molecules is close to the geometric mean of the attractions between the like pairs. No similar relationship holds for the repulsive contribution to the energy of interaction although combining rule 3.2.4. is exact for rigid spheres.

Experimental evidence, including measurements of the second virial coefficients of gaseous mixtures[23] and the coefficients of interdiffusion[12] which are both directly related to ε^*_{12}, has provided the main experimental justification for the combining rules. A major difficulty preventing direct tests of the validity of 3.2.3. and 3.2.4. is that most measured properties of mixtures depend on the like as well as the unlike interactions, and the desired quantity relating to the unlike interaction is thus only a part of the quantity which is experimentally determined. The interdiffusion coefficient D_{12}, does not possess this disadvantage[13] and so may be used to determine ε^*_{12} and r^*_{12} directly.

The combining rules are thus largely empirical and can be expected to apply only to near spherical molecules of similar size. The case of r-mer molecules is much less simple and will be discussed later.

An improved dispersion-forces combining rule has recently been suggested which has been fairly successful in estimating the energy of interaction between molecules of different types.[24]

3.3. The Principle of Corresponding States.

Several modern approaches to the theory of liquid mixtures embody the principle of corresponding states in order to relate the thermodynamic properties of the liquid mixture to those of the pure liquids. The classical principle of corresponding states was originally stated by Van der Waals and was based upon his equation of state. Van der Waals stated that all substances should follow the same equation of state when the pressure, temperature and volume were reduced by the appropriate critical constants. This may be written,

$$\tilde{p} = \tilde{p}'(\tilde{T}, \tilde{v}) \qquad 3.\ 3.\ 1.$$

where $\tilde{p} = \frac{p}{p_c}$, $\tilde{T} = \frac{T}{T_c}$, $\tilde{v} = \frac{v}{v_c}$,

$\tilde{p}'$ is a universal function of the reduced variables $\tilde{T}$ and $\tilde{v}$ and the subscript c refers to the critical point. It was found that the classical principle of corresponding states applied rigorously only to the inert gases and to simple non-polar molecules.

Recently a number of attempts have been made to place the principle of corresponding states on a surer basis than the Van der Waals equation of state, and to extend its usefulness to classes of substances not covered by the classical statement of the principle.

The majority of the modern treatments are based upon that put forward by Pitzer. The assumptions on which his treatment is founded are as follows

1. The partition function Z is taken as the product of the translational, configurational and internal contributions.

2. The translational and configurational partition functions are assumed to be evaluated correctly using classical statistical thermodynamics.

3. The potential energy of the given system is assumed to be the sum of the energies of interaction of all pairs of molecules in the system.

4. The interaction energy ε between any pair of molecules is assumed to be represented by a universal function of the separation r, incorporating two scale factors ε^* and r^* characteristic of the molecular species.

$$\varepsilon = \varepsilon^* \phi\left(\frac{r}{r^*}\right) \qquad 3.\ 3.\ 2.$$

From these four assumptions Pitzer showed by a simple, dimensional analysis that the configurational partition function is a universal function of the reduced variables $\tilde{T} = \frac{kT}{\varepsilon^*}$, $\tilde{v} = \frac{v}{r^{*3}}$

where ε^* and r^* have their previous significance, and k is the Boltzmann constant. If the number of molecules in the system is N, this may be written,

$$Q = r^{*3N}\left[\tilde{q}\left(\frac{kT}{\varepsilon^*}, \frac{v}{r^{*3}}\right)\right]^N \qquad 3.\ 3.\ 3.$$

where $\tilde{q}$ is a universal function of $\frac{kT}{\varepsilon^*}$ and $\frac{v}{r^{*3}}$. This equation leads to a simple expression for the configurational free energy F.

$$F = N f(\tilde{T}, \tilde{v}) \qquad 3.\ 3.\ 4.$$

where f is a universal function of $\tilde{T}$ and $\tilde{v}$.

It can easily be deduced from equation 3.3.4. that an equation of state may be written which involves the temperature, pressure and volume in reduced form. The value of the reduced pressure is $\hat{p} = \frac{p r^{*3}}{\varepsilon^*}$ and the equation of state may be written as

$$\tilde{p} = \tilde{p}''(\tilde{T}, \tilde{v}) \qquad 3.3.5.$$

where $\tilde{p}''$ is a universal function of $\tilde{T}$ and $\tilde{v}$ and depends only on the form of intermolecular potential chosen, i.e. on the form of ϕ chosen in the equation 3.3.2.

When the conditions of the critical point

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 \quad , \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0 \qquad 3.3.6.$$

are applied to equation 3.3.5., it is found that the reduced critical constants $\tilde{p}_c$, $\tilde{T}_c$, and $\tilde{v}_c$ are universal constants, i.e. $\frac{kT_c}{\varepsilon^*}$, $\frac{v_c}{r^{*3}}$ and $\frac{p_c r^{*3}}{\varepsilon^*}$ are universal constants. The following relationships have been shown to hold between the critical constants and the interaction parameters for spherical non-polar molecules.[17]

$$\frac{kT_c}{\varepsilon^*} = 1.25 \qquad 3.3.7.$$

$$\frac{V_c}{Nr^{*3}} = 3.14 \qquad 3.3.8.$$

These relationships can be used to show that the classical statement of the principle of corresponding states is only a particular case of the more general principle given above.

The importance of the principle of corresponding states is that the thermodynamic behaviour of different substances can be reduced to a common basis through the use of reducing parameters derived from molecular properties.

The scope of the principle of corresponding states has been widened considerably from the Pitzer treatment for simple molecules. The behaviour of the following classes of substances has been described using modified versions of the principle of corresponding states.

(a) Very light molecules such as hydrogen and helium are anomalous in their thermodynamic behaviour due to their small mass and weak interaction which permit quantum effects to be significant. These are taken into account in the equation of state through the inclusion of the reduced parameter $\tilde{\lambda} = \frac{h}{r^{*}\sqrt{m\epsilon^{*}}}$.

(b) Substances consisting of large globular molecules deviate from the simple principle of corresponding states by ~~mixture~~ virtue of the non-central character of their interactions, i.e. because a simple two parameter law is incapable of describing their interactions precisely. Trappeniers formulated a principle of corresponding states[26] which incorporated, as additional parameters to $\tilde{T}$ and $\tilde{v}$, the number of peripheral atoms n and the quantity $\tilde{d}$ equal to $\frac{d}{r^{*}}$, where d is a geometric parameter related to the structure of the molecule.

(c) Systems containing polymer molecules obey yet another principle of corresponding states which has been proposed by several authors.[27,28,29] The present research is based on a theory of polymer solutions which utilises this principle of corresponding states for polymers and will be discussed more fully in a later section.

3.4. Theories of Simple Liquid Mixtures

Throughout the past twenty-five years there has been great activity in the field of liquid mixtures and a number of theories have emerged which describe the properties of mixtures of different types of non-polar liquids. A selection of some of these will be discussed in this section; the choice of theory to be discussed has been governed by the following considerations. Only those theories which are based upon molecular properties and not upon empirical classification of solutions, and which allow explicit values of the excess functions of mixing to be calculated through the use of the configurational partition function will be described. These restrictions exclude the Hildebrand theory of regular solutions[30,31] and the Kirkwood theories based upon molecular distribution functions.[11] Each theory will be discussed in terms of the assumptions implicit in its detailed treatment and its main successes and shortcomings will be noted. No detailed account of mathematical derivations will be given.

The most general theory of liquid mixtures yet developed which is founded on a consideration of intermolecular forces, is the conformal solution theory described by Longuet-Higgins.[37] This theory does not require a detailed description of the liquid state and is derived from dimensional arguments. The theory assumes that the components of the mixture, and the mixture itself, obey the same principle of corresponding states, also that the combining rule relating to the characteristic distance r^* for the various types of interaction is valid (equation 3.2.4.). The properties of the mixture are described in terms of a reference substance whose thermodynamic properties are known; one of the pure components is generally chosen as the reference substance. The expressions for the excess functions contain only first order terms in the differences $(\epsilon_{22}^* - \epsilon_{11}^*)$, $(r_{22}^* - r_{11}^*)$ etc. and the main conclusions of the theory are that the volume and heat of mixing should display the same sign and should be proportional to a difference quantity d_{12}.

Experimentally, however, it is known that the excess functions of mixing of many binary systems do not display this simple behaviour, for example in the system neopentane + carbon tetrachloride, h^e is positive and v^e is negative.[33,34,35.] A theory restricted to first order terms is unable to describe the mixing properties of real mixtures such as this. Unfortunately, the inclusion of higher order terms than the first, destroys the main advantage of the conformal solution approach which is the absence of a need for detailed description of the liquid state, since it has been shown that the inclusion of second and higher order terms requires a statistical model.[36] The main value of the conformal solutions theory is that it evaluates correctly the first order terms in all the later, more detailed treatments and thus provides a check on their development.

The group of theories of liquid mixtures which have been brought to the greatest degree of refinement are those based upon the quasi-crystalline model of the liquid state. These have been described in great detail by Guggenheim in his monograph "Mixtures".[22] This type of theory depends on the following assumptions about the mixture; the molecules of the two components are assumed to be of sufficiently equal size and shape that they may be considered to occupy single sites upon a rigid quasi-crystalline lattice; the number of nearest neighbours Z surrounding each molecule is thus taken as constant and the translational motion of the molecules is neglected. These assumptions form the basis of the class of liquid mixtures called strictly regular solutions by Guggenheim.

The configurational partition function includes two quantities upon which the mixing properties of the solution depend. The first is the so-called interchange energy ω, which is the energy gained on mixing by the creation of two 1 - 2 interactions at the expense of destroying one 1 - 1 and one 2 - 2 interactions. The second quantity is the combinatory factor $g(N_1N_2N_{12})$ which is the total number of arrangements of the N_1 molecules of component 1, and N_2 molecules of component 2 on the $(N_1 + N_2)$ lattice sites to give N_{12} pairs of nearest neighbours. If the molecules can be assumed to be randomly distributed over the available lattice sites then the combinatorial factor is readily shown to take the form

$$g(N_1, N_2, N_{12}) = \frac{(N_1+N_2)!}{N_1!\,N_2!} \qquad 3.4.1.$$

The non-random distribution of molecules has been studied in various modifications of the simple lattice theory, the most widely used of these being the first quasi-chemical approximation described by Guggenheim.

The main success of the quasi-crystalline theory has been the evaluation of the combinatory factor for a number of useful situations. For example the evaluation of g for polymer solutions leads to the well known expression for the entropy of mixing of polymer-monomer solutions derived by Flory.

$$S^m = -Nk\,(x_1 \ln \phi_1 + x_2 \ln \phi_2) \qquad 3.4.2.$$

where ϕ_1 is the volume fraction of component 1 in the mixture.

The drawbacks of the theory are principally that it is based upon a physically unrealistic picture of the liquid state; also the comparison of the predicted excess functions with experimental values for systems containing molecules of similar size has shown that the predicted excess entropy is too small and thus $g^e \simeq h^e$, which is not generally found in practise. The assumption of a rigid lattice does not permit the prediction of any quantities related to the equation of state, e.g. v^e, compressibility.

An approach to a theory of liquid mixtures which does not rely on such an unrealistic physical model is afforded by the various cell theories.[12] These theories for liquid mixtures are based on the Lennard-Jones and Devonshire[37,38] theory of pure liquids. In this theory, each molecule of the liquid is assumed to be located in a cell formed by its nearest neighbours with which it interacts according to the Lennard-Jones (12 - 6) potential described in the last section. The configurational partition function Q of the pure liquid is given in this theory by

$$Q = \psi^N \exp\left(-\tfrac{1}{2} N \omega(0)/kT\right) \qquad 3.4.3.$$

where ψ is the partition function of the cell, N is the number of molecules and $-N\omega(0)$ is the potential energy of the system when all the particles are at the centre of their cells. This treatment of the thermodynamic properties of pure liquids is fairly successful but suffered from the drawback that the regularity of the structure of the liquid, which is demanded by the existence of cells, causes the degree of order to be greatly overestimated. The result of this overestimation of the degree of order is to produce an underestimation of the entropy of the liquid by an amount which has come to be known as the communal entropy.[12] Various modifications to the original Lennard-Jones and Devonshire model to account for this poor estimate of the entropy have been made. These include multiple occupancy of cells, the presence of unoccupied cells and the existence of clusters of cells. While many of these variations of the original cell theory correctly estimate the entropy of a liquid, at least in principle, they have added greatly to the complexity of the original theory and have not been used to any extent in liquid mixture theories.

The extension of the cell model for pure liquids to mixtures of liquids was first made by Prigogine.[38,39,40] The assumptions are the same as those for pure liquids with the addition that the parameter ε^* in the interaction law is replaced by the composition dependent parameters $\langle \varepsilon_1^* \rangle$ and $\langle \varepsilon_2^* \rangle$, for the interactions of molecules of components 1 and 2 respectively. These are given by the following expressions if random mixing is assumed,

$$\langle \varepsilon_1^* \rangle = x_1 \varepsilon_{11}^* + x_2 \varepsilon_{12}^* \qquad 3.4.4.$$

$$\langle \varepsilon_2^* \rangle = x_2 \varepsilon_{22}^* + x_1 \varepsilon_{12}^* . \qquad 3.4.5.$$

When this substition has been made, the configurational partition function of a mixture of components 1 and 2 of equal size is given by the following expression,

$$Q = \frac{(N_1 + N_2)!}{N_1!\,N_2!}\;\psi_1^{N_1}\,\psi_2^{N_2}\;\exp\left[\frac{-(N_1\omega_1(0) + N_2\omega_2(0))}{kT}\right] \qquad 3.\ 4.\ 6.$$

ψ is the cell partition function for a cell containing a molecule 1 and $-N_1\omega_1(o)$ is the lattice energy of pure I etc. The thermodynamic functions of mixing are obtained from this equation. In order to reduce the number of variables in the final explicit equations, the following parameters are introduced,

$$\delta = \frac{1}{\varepsilon^*_{11}}\left(\varepsilon^*_{22} - \varepsilon^*_{11}\right) \qquad 3.\ 4.\ 7.$$

$$\theta = \frac{1}{2\varepsilon^*_{11}}\left[2\varepsilon^*_{12} - (\varepsilon^*_{11} + \varepsilon^*_{22})\right] \qquad 3.\ 4.\ 8.$$

The parameter θ is closely related to the interchange energy of the strictly regular solution

$$\omega = \theta\,\varepsilon^*_{11} \qquad 3.\ 4.\ 9.$$

It is clear that the use of δ and θ relates the values of the interaction constants of the mixture to those of the reference substance 1. The theory was originally applied to mixtures of components of equal size by Prigogine and his co-workers but it has since been extended to include the treatment of mixtures of molecules of different size.[40,42] The difference in size is introduced into the final ezpressions for the excess functions through the quantity defined by the following equation

$$\rho = \frac{1}{r^*_{11}}\left(r^*_{22} - r^*_{11}\right) \qquad 3.\ 4.\ 10.$$

In effect, the theory treats the mixture as a pure liquid with composition dependent interaction parameters of the form $\langle \varepsilon^*_1 \rangle$ etc. The principal value of the cell theory of mixtures is that it relates the properties of the mixture to small differences in the intermolecular interaction.

Its consistency is checked by the fact that to a first approximation the cell theory leads to the same results for the excess functions as conformal solutions theory.

The assumption of random mixing which is used in the cell theory for mixtures of molecules of similar size, has been justified by Prigogine and Garikian.[43] Their findings have been confirmed by Brown,[44] who points out however, that this assumption cannot be expected to hold for mixtures of molecules of greatly differing size.

The cell theory has had great success in predicting the behaviour of mixtures of non-polar molecules but its dependence on an inexact theory of pure liquids and the approximations required to deal with mixtures of molecules of different size are very unsatisfactory features.

A theory of liquids mixtures which does reduce to an exact theory for pure liquids while retaining the more desirable features of the cell theory is the corresponding states, average potential theory which was introduced independently and almost simultaneously by Prigogine,[45] Scott[47] and Brown.[48] The treatments described by these authors are very similar. The principal variations are these, Brown shows that no reference to a cell type of model is necessary and develops his treatment on the principal assumption that the mixture is completely random, and Scott in his treatment bases the behaviour of the mixture on the properties of both pure components and not on a single reference component as is the case in the Prigogine and Brown treatments.

The version of the theory to be described here is that presented by Prigogine,[49,46] and in this section and in the section on polymers the nomenclature is that which he used. The assumptions required in the theory are the following.

1. The pure components and the mixture obey the same principle of corresponding

states.

2. The configurational partition function, Q, is written in the form,

$$Q = g(N_1, N_2, N_{12})\langle r_1^*\rangle^{3N_1}\langle r_2^*\rangle^{3N_2}\left[q(\langle\tilde{T}_1\rangle,\langle\tilde{V}_1\rangle)\right]^{N_1}\left[q(\langle\tilde{T}_2\rangle,\langle\tilde{V}_2\rangle)\right]^{N_2} \qquad 3.\ 4.\ 11.$$

where g is the combinatory factor, and q is the same function as for pure substances. The reduced quantities $\langle\tilde{T}_1\rangle$ etc. will be described shortly.

3. The interactions between unlike molecules follow the same form of potential as those between like molecules using average composition-dependent interaction parameters.

The values of the interaction parameters depend on the type of pair potential chosen and it has been shown that only a potential of the Lennard-Jones bireciprocal type is suitable for the average-potential type of treatment. The average interaction parameters are written as $\langle\varepsilon_1^*\rangle$, $\langle\varepsilon_2^*\rangle$, $\langle r_1^*\rangle$, and $\langle r_2^*\rangle$ and these lead to values of the reduced parameters shown below.

$$\langle\tilde{T}_1\rangle = \frac{kT}{\langle\varepsilon_1^*\rangle} \qquad \langle\tilde{V}_1\rangle = \frac{a_1^3}{\gamma\langle r_1^*\rangle^3} \qquad 3.\ 4.\ 12.$$

where γ is a geometrical constant and a_1 is an average distance between a molecule of component 1 and its neighbours.

It can be seen that the expression for the configurational partition function 3.4.11. reduces to the same value as for a pure substance, and so the theory differs from the cell treatment in that it is based upon an exact treatment of the pure liquid state.

The excess free energy of the mixture is obtained from the configurational partition function. The final explicit equation is fairly lengthy and is not quoted here. It is found to contain thermodynamic properties of the pure reference substance which is generally chosen to be one of the components of the mixture. The parameters θ, δ and ρ which were defined during the description of the cell theory also appear in the final expressions.

The values of the parameters δ and ϵ can be obtained from properties of the pure substance;[50] θ which depends on the value of ϵ_{12}^{*}, the interaction energy between the unlike pair of molecules, is more difficult to evaluate. When it can be assumed that the forces between the molecules are principally of the dispersion force type and the combining rule 3.2.3. holds, it is readily shown that

$$\theta = -\frac{\delta^2}{8}$$

For other cases, θ is generally taken to be an adjustable parameter and is varied to give the best agreement with several sets of experimental results.

The other excess functions are obtained by appropriate differentiation of the excess free energy.

The numerical results obtained from the theory are very dependent on the accuracy with which the thermodynamic properties of the reference component are known. In some cases it is found that even the choice of reference component affects the predictions of the theory greatly.[57] The use by Scott of interaction parameters which are symmetrically dependent on both components, unlike those of Prigogine, avoids this problem.

A test of the average potential theory has been obtained by comparing the observed and predicted values of the excess functions of some systems of mixtures of quasi-spherical molecules of nearly equal size.[51,50] In nearly all cases good qualitative agreement is found. In a few cases the quantitative agreement is good also, and is generally superior to that obtained from the cell model.

The development of the theory has permitted its extension to two special cases, namely mixtures of isotopes, e.g. the system $He^3 + He^4$ for which an upper critical solution temperature was predicted[52] before being observed experimentally by Walters and Fairbank,[53] and solutions of polymer or r-mers which were previously discussed in terms of the lattice model. This development will be treated in more detail in the next section.

An interesting feature of the numerical results of the average-potential theory concerns the excess volume of mixing. Mixtures formed from molecules of equal size should display contraction while mixtures of molecules of slightly different size should display dilatation. This has been found to be the case, e.g. neopentane + cyclohexane for which $\rho = 0.00$, has $v^e < 0$,[33] and

cyclohexane + cyclopentane for which $\rho = 0.05$, has $v^e > 0$.[50]

3.5. Theories of Liquid Mixtures of Polymers.

The theoretical treatment of the thermodynamic behaviour of solutions of polymer molecules has been discussed by many authors on the basis of the quasi-crystalline lattice approach.[27.] The results of this treatment have been fairly successful but the assumptions on which the theory has been built suffer from two drawbacks. Firstly the polymer molecules which are considered as being divided into a number r of identical segments, are assumed to occupy r sites on a rigid quasi-crystalline lattice. This requires that the segments of the polymer and the other component (which we shall hereafter take to be the monomer) are of closely similar size, also that thermal expansion and expansion on mixing should be neglected. This is a drawback shared by the lattice theory of mixtures of molecules of nearly equal size. The second weakness is that the structure of the r-mer molecule is largely ignored although Rushbrooke has suggested a method whereby effects of flexibility in the r-mer chain can be incorporated into the theory.[55.]

The principal success of the quasi-crystalline theories of r-mer solutions has been the correct evaluation of the combinatorial factor. The values of the combinatorial factor obtained using the lattice theories have been used in several subsequent treatments of r-mer solutions.

An improved theory was suggested by Prigogine[56,57] based upon an extension of the cell theory of mixtures of molecules of nearly equal size. This treatment suffers from the same drawbacks shown by the original cell theory, and it has been superceded by Prigogine's most recent treatment of r-mer solutions which is based upon an average-potential, corresponding-states type of theory.[54]

The starting point in the latest Prigogine treatment is the formulation of a theorem of corresponding states for pure polymers.[27] This is acheived by introducing a number of parameters which describe the structure of the polymer molecules. It is assumed that each polymer molecule is divided into r identical segments, each occupying a single site on a quasi-crystalline lattice and that it interacts with neighbouring segments of adjacent polymer molecules through qz nearest neighbour contacts where z is the coordination number of the type of lattice chosen and q is obtained from the relationship,

$$qz = rz - 2r + 2 \qquad 3.\ 5.\ I.$$

or

$$q = r - \frac{(2r-2)}{z} \qquad 3.\ 5.\ 2.$$

The polymer molecule is taken to be a dynamical system possessing 3r degrees of freedom. The external degrees of freedom, which depend on the intermolecular forces, are separated from the internal degrees of freedom which are related to the valency forces. The justification for this separation is that the order of magnitude of the two kinds of forces are very different. The configurational partition function depends only on the external degrees of freedom, the number of which is designated 3c. The configurational partition function is evaluated in the form,

$$Q = g \cdot r^{*3Nc} \, q(\hat{T}, \hat{v})^{Nc}. \qquad 3.5.3.$$

where g is the combinatorial factor, N is the number of polymer molecules, q is the same function of the reduced temperature and volume as for monomer molecule systems and r^* is the interaction constant characteristic of the molecular species. The reduced variables T and v are defined by the following equations

$$\tilde{T} = \frac{ckT}{q\epsilon^*} \qquad 3.5.4.$$

$$\hat{v} = \frac{V}{Nr}\left(\frac{1}{r^*}\right)^3. \qquad 3.5.5.$$

where ϵ^* add r^* are the characteristic interaction energy and separation and V is the volume of the system of N molecules, $\tilde{v}$ may be considered as a reduced volume per segment.

It is found that the ratio $\frac{\epsilon}{q}$ which enters the definition of the reduced temperature is related directly to the structure of the molecule and it is through this quantity that the excess functions of mixing of polymer solutions depend on the struature of the components of the mixture.

A direct consequence of the form of the configurational partition function is the emergence of a reduced equation of state,

$$\hat{p} = \tilde{p}'''(\hat{T}, \tilde{v}) \qquad 3.5.6.$$

where the reduced pressure p is defined as

$$\hat{p} = p \cdot \frac{r}{q} \cdot \frac{r^{*3}}{\epsilon^*} \qquad 3.5.7.$$

and $\tilde{p}'''$ is a universal function of $\hat{T}$ and $\tilde{v}$ which depends on the structure of the polymer molecule only through the introduction of the quantities r, q and c into the definitions of the reduced variables. It should thus be a function similar to that for monomer molecules.

The validity of the reasoning which leads to 3.5.6. has been tested by Prigogine[27] and Hijmans[28] using physical properties of the homologous series of alkanes C_nH_{2n+2} up to the substance $C_{64}H_{130}$. The results of this test appear to confirm the assumptions and treatment used.

The principle of corresponding states for r-mer molecules is extended to the case of mixtures of polymers in a completely straightforward manner. The configurational partition function for the mixture is written in the form

$$Q = q . \langle r_1^* \rangle^{3Nc_1x_1} \langle r_2^* \rangle^{3Nc_2x_2} \; q(\langle \tilde{T} \rangle, \langle \tilde{v} \rangle)^{\bar{z}} \qquad 3.\ 5.\ 8.$$

where $\langle r_1^* \rangle$ is an average interaction distance, q is a universal function of the reduced temperature and pressure and is the same as that for monomer molecules. The average reduced temperature is defined as

$$\langle \tilde{T} \rangle = \frac{kT}{\langle \varepsilon^* \rangle} \left\langle \frac{c}{q} \right\rangle \qquad 3.\ 5.\ 9.$$

where the average interaction energy $\langle \varepsilon^* \rangle$ is given by the following expression using the assumption of random mixing

$$\langle \varepsilon^* \rangle = X_1 \langle \varepsilon_1^* \rangle + X_2 \langle \varepsilon_2^* \rangle \qquad 3.\ 5.\ 10.$$

and $\left\langle \frac{c}{q} \right\rangle$ is defined by the equation

$$\left\langle \frac{c}{q} \right\rangle = \frac{x_1c_1 + x_2c_2}{x_1q_1 + x_2q_2} = X_1\left(\frac{c_1}{q_1}\right) + X_2\left(\frac{c_2}{q_2}\right) \qquad 3.\ 5.\ 11.$$

The quantities X_1 and X_2 are surface fractions defined by

$$X_i = \frac{q_i x_i}{\Sigma q_i x_i} \qquad 3.\ 5.\ 12.$$

and these assume the significance of the mole fraction in the original theory.

The final values of the excess functions are obtained using these expressions, the interaction parameters θ, δ and ρ which have been defined previously and a Lennard-Jones type of pair potential for the interactions between the segments of adjacent r-mer molecules.

It is found from the final explicit expressions, that the excess functions arise from three sources.

1. The geometrical effect which is caused by the different size of molecules 1 and 2. This is accounted for in the calculation of the combinatory factor g using one of the methods originally derived using the rigid lattice model.

2. The energetical effect which arises from the differing interaction energies for the types of interaction involved, viz., ε_{11}^*, ϵ_{22}^*, ε_{22}^*. These are included in the final expressions through the use of Θ, δ and ρ.

3. The structural effect, which is a result of the differing structures of the component molecules, is described in terms of the ratios $\frac{c_1}{q_1}$ and $\frac{c_2}{q_2}$.

The excess functions depend on a larger number of variables and are consequently expressed in a much more complicated form than those obtained using the same type of average-potential, corresponding-states treatment; for mixtures of molecules of nearly equal size.

The simplest case which is normally considered is that of a mixture of a monomer 1 with an r-mer 2. In this case $r_1 = q_1 = c_1 = 1$ and r_2, q_2 and c_2 are determined form the structure of the r-mer molecule.

The explicit expressions for all the excess functions are very complex and the expression for the excess volume of mixing alone, which is of principal interest in the present work, is given here. (eqation 17.7.1, p. 363, Reference 2)

The properties of the pure reference substance 1 which are required are the molar volume v_1 and its first and second derivatives with respect to temperature, $\frac{dv_1}{dT}$ and $\frac{d^2v_1}{dT^2}$ at the temperature of mixing T.

$$\begin{aligned} v^e = {} & \frac{v_1}{r_1}\left[x_1 r_1\left(\frac{\langle r_1^*\rangle^3}{r_{11}^{*3}} - 1\right) + x_2 r_2\left(\frac{\langle r_2^*\rangle^3}{r_{11}^{*3}} - \frac{r_{22}^{*3}}{r_{11}^{*3}}\right)\right] \\ & + \frac{T}{r_1}\frac{dv_1}{dT}\left[\left(x_1 r_1 \frac{\langle r_1^*\rangle^3}{r_{11}^{*3}} + x_2 r_2 \frac{\langle r_2^*\rangle^3}{r_{11}^{*3}}\right)\left(\frac{\varepsilon_{11}^*}{\langle\varepsilon^*\rangle}\,\frac{\bar{c}}{\bar{q}}\cdot\frac{q_1}{c_1} - 1\right)\right. \\ & \qquad \left. - x^2 r_2 \frac{r_{22}^{*3}}{r_{11}^{*3}}\left(\frac{\varepsilon_{11}^*}{\varepsilon_{22}^*}\cdot\frac{c_2}{q_2} - 1\right)\right] \\ & + \frac{1}{2}\frac{T^2}{r_1}\frac{d^2v_1}{dT^2}\left[\bar{r}\left(\frac{\bar{c}}{\bar{q}}\cdot\frac{q_1}{c_1}\cdot\frac{\varepsilon_{11}^*}{\langle\varepsilon^*\rangle} - 1\right)^2 - x_2 r_2\left(\frac{c_2}{q_2}\,\frac{q_1}{c_1}\,\frac{\varepsilon_{11}^*}{\varepsilon_{22}^*} - 1\right)^2\right] \qquad 3.\ 5.\ 13. \end{aligned}$$

The terms $\frac{\langle r_1^*\rangle^3}{r_{11}^3}$ etc. are functions of the parameters θ, δ and ρ.

$$\frac{\langle r_1^*\rangle}{r_{11}^*} = 1 + \frac{1}{2}\rho x_2\left[1+\left(\theta+\frac{\delta}{2}\right)x_1 + \frac{17}{4}x_1\rho\right]$$

$$\frac{\langle r_2^*\rangle}{r_{11}^*} = 1 + \rho - \frac{1}{2}\rho x_2\left[1+\left(\theta-\frac{1}{2}\delta\right)x_2 - \frac{17}{4}x_2\rho\right]$$

$$\frac{\langle \varepsilon^*\rangle}{\varepsilon_{11}^*} = 1 + \delta x_2 + (2\theta - 9\rho^2)x_1x_2$$

$$\frac{\varepsilon_{22}^*}{\varepsilon_{11}^*} = 1+\delta \qquad \frac{r_{22}^*}{r_{11}^*} = 1+\rho$$

There has been little direct evidence to assess the value of the theory but it has been shown that the inversion of the excess functions discovered by Everett and Swinton for the system benzene-diphenylmethane can be fairly satisfactorily accounted for using reasonable values of θ, δ and ρ. At present this constitutes almost the only direct evidence of the applicability of the average-potential, corresponding states type of approach to mixtures of r-mer molecules.

The equation 3.5.13. can be differentiated with respect to temperature to give $\frac{dv^e}{dT}$, the only fresh property of the reference substance which appears being $\frac{d^2v_1}{dT^3}$. The explicit expression is given below.

$$\begin{aligned}\frac{dv^e}{dT} = {} & \frac{1}{r_1}\frac{dv_1}{dT}\left[x_1 r_1\left(\frac{\langle r_1^*\rangle^3}{r_{11}^{*3}}-1\right) + x_2 r_2\left(\frac{\langle r_2^*\rangle^3}{r_{11}^{*3}} - \frac{r_{22}^{*3}}{r_{11}^{*3}}\right)\right] \\ & + \frac{1}{r_1}\left[T\frac{d^2v_1}{dT^2} + \frac{dv_1}{dT}\right]\left[\left(x_1 r_1\frac{\langle r_1^*\rangle^3}{r_{11}^{*3}} + x_2 r_2\frac{\langle r_2^*\rangle^3}{r_{11}^{*3}}\right)\left(\frac{\varepsilon_{11}^*}{\langle\varepsilon^*\rangle}\frac{\bar{c}}{\bar{q}}\frac{q_1}{c_1}-1\right)\right. \\ & \left. - x_2 r_2\frac{r_{22}^{*3}}{r_{11}^{*3}}\left(\frac{\varepsilon_{11}^*}{\varepsilon_{22}^*}\cdot\frac{c_2}{q_2}\frac{q_1}{c_1}-1\right)\right] \\ & + \frac{1}{2r_1}\left[T^2\frac{d^3v_1}{dT} + 2T\frac{d^2v_1}{dT^2}\right]\left[\bar{r}\left(\frac{\bar{c}}{\bar{q}}\frac{q_1}{c_1}\frac{\varepsilon_{11}^*}{\langle\varepsilon^*\rangle}-1\right)^2 - x_2 r_2\left(\frac{c_2}{q_2}\frac{q_1}{c_1}\frac{\varepsilon_{11}^*}{\varepsilon_{22}^*}-1\right)^2\right]\end{aligned}$$

3.6. The Reasons for the Present Research.

It has been pointed out by Prigogine that if a mixture of the monomer-r-mer type is considered, in which the r-mer chain length can be increased smoothly, the excess volume of mixing should exhibit periodic behaviour with minima when the size of the r-mer molecule is approximately an integral multiple of that of the monomer. i.e. r_2 = integer and $\rho = 0$. This may be shown graphically by plotting v^e against the size parameter ρ for constant values of δ and θ. The curves obtained show minima around small values of ρ. The value of v^e for $\rho = 0$ is negative for most values of δ. When $|\rho|$ is increased this contraction is transformed into an increase in volume. The situation is thus formally similar to that of mixtures of molecules of similar size for which a negative v^e is expected for mixtures of molecules of equal size and a positive v^e for mixtures of molecules of slightly differing sizes.

No systematic study has been carried out to provide experimental verification of this prediction which is a direct test of the quasi-crystalline treatment of polymer solutions. It is the principal purpose, object of the present research to fill this gap. The intention has been to determine the excess volume of mixing of a set of systems of the monomer-r-mer type, in which the size of the r-mer molecule varies from a value somewhat less than twice that of the monomer to a value slightly more than twice that of the monomer. In the set of systems chosen, the monomer component 1 is cyclohexene and the r-mer molecules or components 2, in increasing order of size are t-butylcyclohexene, dicyclohexyl, dicyclohexylmethane, 1,2-dicyclohexylethane and 1,3-dicyclohexylpropane. The ratio of the molar volumes of dimer and monomer is given in Table 3.6.1.

Table 3.6.1.

System.	$\left(\frac{V_2}{V_1}\right)$ 20°C.
Cyclohexane + t-Butylcyclohexane	1.602
Cyclohexane + dicyclohexyl	1.760
Cyclohexane + dicyclohexylmethane	1.907
Cyclohexane + 1,2-dicyclohexylethane	2.056
Cyclohexane + 1,3-dicyclohexylpropane	2.213

It was hoped that the choice of a set of monomer-dimer systems of closely related chemical structure and properties would reduce the variations in δ and θ between the different systems and thus isolate the dependence of v^e on the values of ρ. It will be seen that the δ values which were obtained from the temperature dependence of the molar volumes of the components confirmed the constancy of δ expected, while the range of values of ρ were fairly well distributed about $\rho = 0$.

The Models of the various types of molecules were made using a set of Courtaulds Molecular Models. The near spherical shape of the cyclohexane molecule was confirmed. The dimer molecules were sausage-shaped and their arbitrary division into two segments was seen to be fairly justifiable.

A further consequence of the choice of dimer molecules is that the deviations from the principle of Corresponding States should be similar and thus the final results should be free of errors from this source.

It was also intended to test the general validity of the theory by comparing the values of the excess volume of mixing, v^e, obtained from the theory with experiment and the theoretical $\frac{dv^e}{dT}$ with the experimental values.

A consequence of the similar chemical nature of the mixtures studied, was that the deviations from ideality should be small, and it was therefore thought that it should be possible to predict the values of the excess functions with confidence.

CHAPTER 4.

Description of the Apparatus.

1. Introduction. The methods of measuring the excess volume of mixing of binary liquid mixtures fall into two broad groups, which may be called the classical and the direct methods.

The classical method requires the determination of the densities of the pure, unmixed components of the system and of several mixtures of known composition.[59-70] The excess volume of mixing is then found from the expression,

$$V^E = \left(\frac{x_1M_1 + x_2M_2}{d_m}\right) - \left(\frac{x_1M_1}{d_1} + \frac{x_2M_2}{d_2}\right) \qquad 4.1.1.$$

where M_1 and M_2 are the gram-molecular weights of components 1 and 2 and d_1, d_2 and d_m are the densities of the pure components and of the mixture of composition X_1.

In the case of mixtures of non-polar liquids, the two quantities within the brackets in equation 4.1.1. are generally found to be of almost equal magnitude and thus the accuracy of the value of V^E is very susceptible to errors in the determination of the densities. For example, in the system cyclohexane and dicyclohexyl, it is found that a precision of 1 part in 10,000 in the density determinations is required to give a precision of 20% in V^E. The composition of the mixture must also be known accurately. This can present difficulty especially if the densities are determined pyknometrically and one of the components of the mixture is much more volatile than the other. In these circumstances, changes in the composition of the mixture are liable to arise during filling of the pyknometer. Another requirement is that the different density determinations must be made at exactly the same temperature.

The merits of the classical method are that it is straightforward and requires fairly simple apparatus. Its drawbacks are that errors are likely if all the possible sources of error noted above are not eliminated.

The direct method involves the measurement of the volume change ΔV which takes place when known masses m_1 and m_2 of the two pure components are mixed at constant temperature and pressure.[71-77] The excess volume of mixing is then calculated from the expression,

$$V^e = \frac{\Delta V}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \qquad 4.1.2.$$

The volume change ΔV is usually obtained by following the movement of a mercury meniscus in a graduated capillary. This method has the advantage of requiring fewer separate measurements than the classical method.

It is a drawback of both the classical and the direct methods that each determination yields information about V^e at a single composition only. The determination of V^e over the full composition range at a given temperature is therefore a fairly lengthy process and requires substantial quantities of pure materials. Most investigations consequently result in only a few measurements at each temperature.

The method empolyed in the present work does not suffer from these drawbacks. The apparatus used is similar to that described by Desmyter and van der Waals,[77] which in turn was based upon an instrument described by Geffcken, Kruis and Solana.[78] The principle of the method is that a known quantity of one component of the mixture is successively diluted with increasing, known quantities of the other component, and the volume change occurring at each stage is measured directly.

The advantages of this method are:-

1. A relatively small quantity of each material is required to investigate v^e over the full composition range. This was of particular advantage in the present work because certain of the dimer-compounds were available in only limited amount.

2. The measurements of v^e are more accurate and can be extended to cover the composition range more quickly and more fully than those obtained by any other means.

3. The liquids are confined within mercury or glass surfaces without a vapour space. The composition of the solution is thus unaffected by the relative volatilities of the components.

The rate of change of v^e with temperature, $\frac{dv^e}{dT}$, is generally determined by measuring v^e at different temperatures. Since $\frac{dv^e}{dT}$ is usually sensibly constant over small temperature ranges, it may be obtained from measurements of v^e at two temperatures only.

Another method of determining $\frac{dv^e}{dT}$ involves a dilatometric technique.[60] The value of v^e is determined at one temperature over the full composition range and then the coefficient of thermal expansion of mixtures of known composition is measured at a series of temperatures. The apparatus used is generally similar to the dilatometer designed by Burlew.[79] This has been modified by a number of later workers.[10,60]

In the present work the former method was employed, v^e being measured at two temperatures and $\frac{dv^e}{dT}$ calculated from the equation,

$$\frac{dv^e}{dT} = \frac{\Delta V^e}{\Delta T} \qquad 4.1.3.$$

where ΔV^e is the difference between the two values of v^e and ΔT is the difference between the temperature at which measurements were made.

4.2. The Dilatometer. The dilatometer which was constructed of borosilicate glass is shown diagrammatically in Figure 4.2.1. It was necessary to know accurately the internal diameter of tube C and capillaries D and E and Veridia precision-bore glass tubing was used for these. Although the bore diameter of this tubing is guaranteed to be within 0.001 cm. of the specified size and needs no calibration, the bore of a sample of the 0.04 cm. nominal internal diameter capillary was measured as a check. This was done by weighing threads of mercury of measured length within the capillary. The mean bore diameter was found to be 0.04005 ± 0.0008 cm.

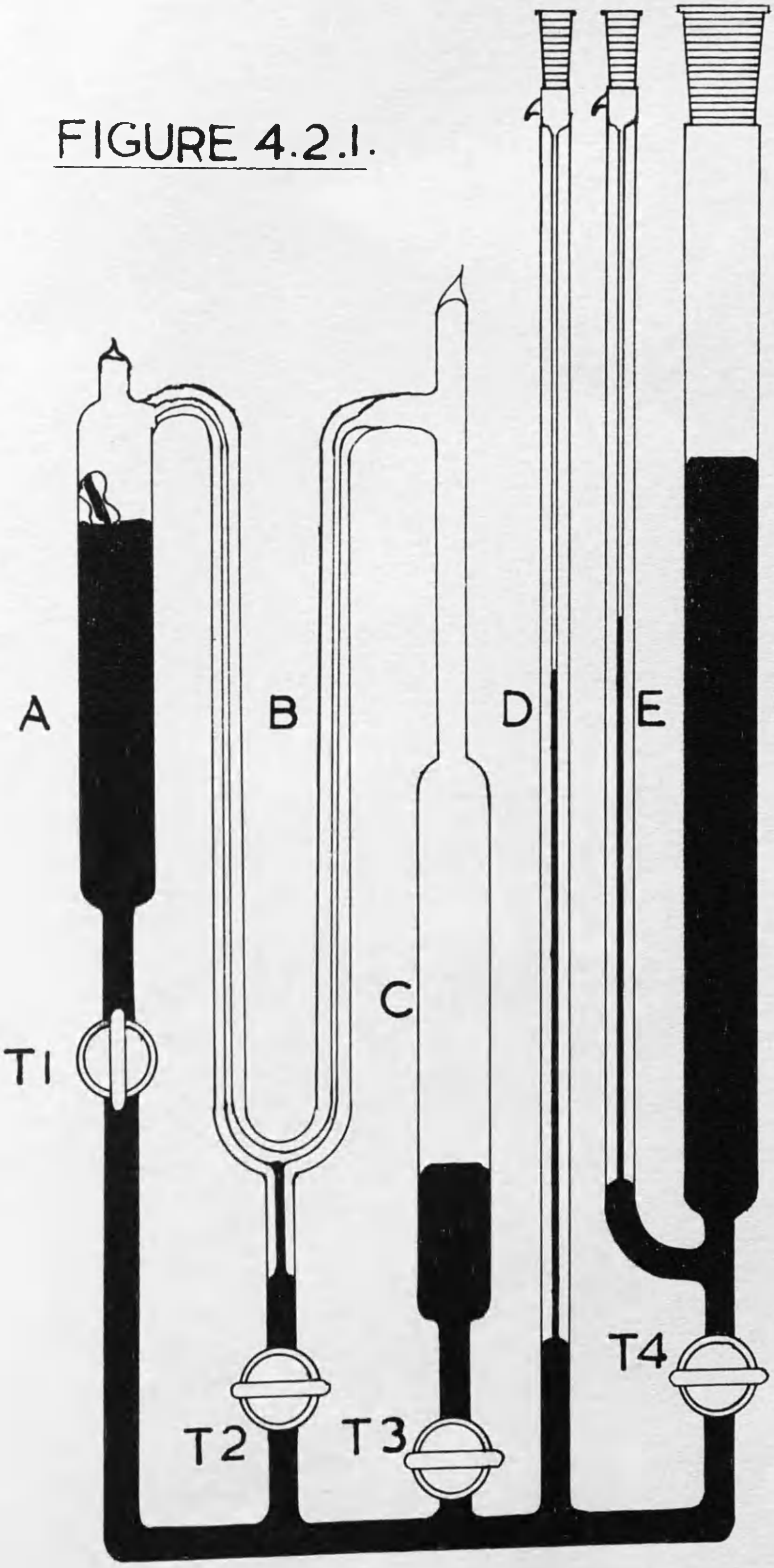
The high vacuum stopcocks T_1, T_2, T_3 and T_4 were never in contact with hydrocarbon liquid and were lubricated with Apiezon "L" grease. This grease softened at 40°C and there was a tendency for the keys of the taps to slide out of the barrels at this temperature. This was prevented by fitting all taps with specially designed copper screw-clips which held the keys firmly.

The details of the design may be best described by describing the method of operation of the dilatometer during an experiment.

Initially tube A contained a known quantity, n_2 moles, of the pure dimer component, tube C contained pure cyclohexane and the remainder of the volume of the dilatometer was occupied by mercury. The mass of dimer component was generally about 3g. The normal position of the taps at this stage, was that T_2, T_3 and T_4 were closed, and T_1, was open.

The mercury surface in tube A was at a higher level than that in tube C, thus on opening T_2 for a short period, mercury flowed from A though T_1 and T_3

FIGURE 4.2.1.



THE DILATOMETER.

into C. An equal volume of cyclohexane from C was displaced through the capillary U-tube B into A where mixing with the dimer component took place.

The liquids in A were mixed using a glass stirrer containing a soft iron core. The stirrer was moved up and down inside the tube by means of a magnet placed immediately outside the tube. The magnet was attached to a long plastic handle which protruded through the cover of the thermostat bath. A Terry clip, attached to the handle adjacent to the magnet, was fitted around tube A and this acted as a guide to keep the magnet moving vertically close to the tube.

All the solutions studied were non-ideal and thus a small volume change ΔV cm.^{3}, took place on mixing. The extent of this volume change was obtained by measuring the position of the mercury surface in capillary D with the cathetometer. The internal diameter of D was 0.04 cm. thus a change in volume of the hydrocarbon liquids of 1.257×10^{-3} cm.^{3} produced a displacement of 1 cm. in the mercury level.

The quantity of cyclohexane entering A was obtained by measuring the displacement of the mercury surface in C using the cathetometer.

A broad Terry clip was placed around C to act as a shield for the mercury meniscus, enabling it to be clearly seen. Its position could be shifted along the tube to follow the meniscus.

The internal diameter of the tube C was 1.500 ± 0.001 cm. and, knowing the density of cyclohexane at the temperature used, the number of moles of cyclohexane, n_1, entering A could be found. Tube C contained 16.35×10^{-3} moles per cm. at 20.00°C and 15.96×10^{-3} moles per cm. at 40.00°C.

The composition of the mixture in A at any stage in the mixing process was obtained from the formula,

$$X_2 = \frac{n_2}{n_1 + n_2}$$

4.2.1.

The corresponding molar excess volume of mixing was calculated from the formula,

$$V^e = \frac{\Delta V}{n_1 + n_2}$$

4.2.2.

The mixing process was continued by adding further cyclohexane using the procedure described above until the mole fraction of the dimer was reduced to approximately 0.1. In this way the excess volume of mixing of the given system could be investigated over almost the full composition range at one temperature, using only 2 - 3 g. of the dimer component.

The pressure at which mixing took place was the hydrostatic pressure at the mercury surface in tube A, (provided that tap T_3 was closed). The pressure was thus greater or less than atmospheric, depending on whether the mercury surface in capillary D which was open to the atmosphere, was higher or lower than that in tube A. During the experiment, the relative positions of these mercury levels altered, and thus the pressure on the hydrocarbon liquids changed. While the value of the excess function V^e is relatively insensitive to the small pressure changes involved, the total volume of the liquids in the dilatometer was liable to vary appreciably because of their compressibility. A method of eliminating variations in the hydrostatic pressure in A during the course of an experiment was therefore necessary. This was carried out by varying the air pressure acting on the mercury surface in D, in such a way that the hydrostatic pressure of the hydrocarbon liquids was constant and equal to atmospheric pressure. Capillaries D and E, were connected through B7 ground glass joints and rubber tubing to a common air reservoir. The air pressure within this was varied by blowing or sucking air through a stopcock until the difference in mercury levels between tubes A and D was equal to that between tubes F and E, as measured using the cathetometer.

In this condition, the hydrostatic pressure in A was equal to the pressure acting on the mercury level in tube F, which being open to the atmosphere was always atmospheric pressure. The condition may be expressed in the relation

$$l_A - l_D = l_F - l_E \qquad 4.2.3.$$

where l_A is the level of the mercury surface in tube A as measured on the cathetometer scale, etc.

The possible effects of unequal capillary depression were minimized by using identical Veridia capillary for D and E. Tubes A and F were sufficiently wide for capillary effects to be negligible.

It has been shown[22] that using a dilatometer of the present design without compensating for changes in the hydrostatic pressure of the organic liquids, apparent volume changes of up to 1.5×10^{-3} % may occur, whereas the above procedure produces constancy in volume to within 0.1×10^{-3} %.

It may be noted that although atmospheric pressure may change during the course of an experiment, its variations are much less than the pressure changes for which compensation has been described, and thus may be neglected.

4.3. The Vacuum Line. The general arrangement of the vacuum line is shown in Figure 4.3.1. It was constructed of borosilicate glass and was mounted on a welded frame-work made up from ½" diameter steel tubing.

The pumping system comprised a two-stage, rotary oil pump backing a two-stage, silicone oil, diffusion pump through a liquid nitrogen cold trap. The vacuum in the system was measured using a Pirani gauge mounted between the rotary pump and the diffusion pump, and a Penning gauge S mounted on the main vacuum line.

The dilatometer was fused to the vacuum line at points G and H.

The vacuum line was used principally for the degassing, storing and introduction into the dilatometer of cyclohexane, the degassing of the dimer component, and the distillation under vacuum of mercury into the dilatometer. The sections which were used for these functions will be described separately.

The cyclohexane treatment section was connected to the main vacuum line through stopcock T_8. Purified cyclohexane was stored over sodium in the pear-shaped reservoir I. This was of 300 cm^3 capacity and was attached to the apparatus through a mercury sealed B 24 joint J. The reservoir could be isolated from the remainder of the system by raising mercury in each limb of the U-tube K. The mercury in K was raised or lowered by admitting air to or evacuating the flask L through tap T_{10}. When it was necessary to maintain a vacuum in the reservoir, while the remainder of the section was at atmospheric pressure, the whole section was evacuated, and the mercury raised in both limbs of the U-tube by admitting air through T_{10}. On closing tap T_9 and then admitting air to the right hand side of the U-tube, the level of the mercury in the left hand limb rose untill the difference in levels was about 76 cm.

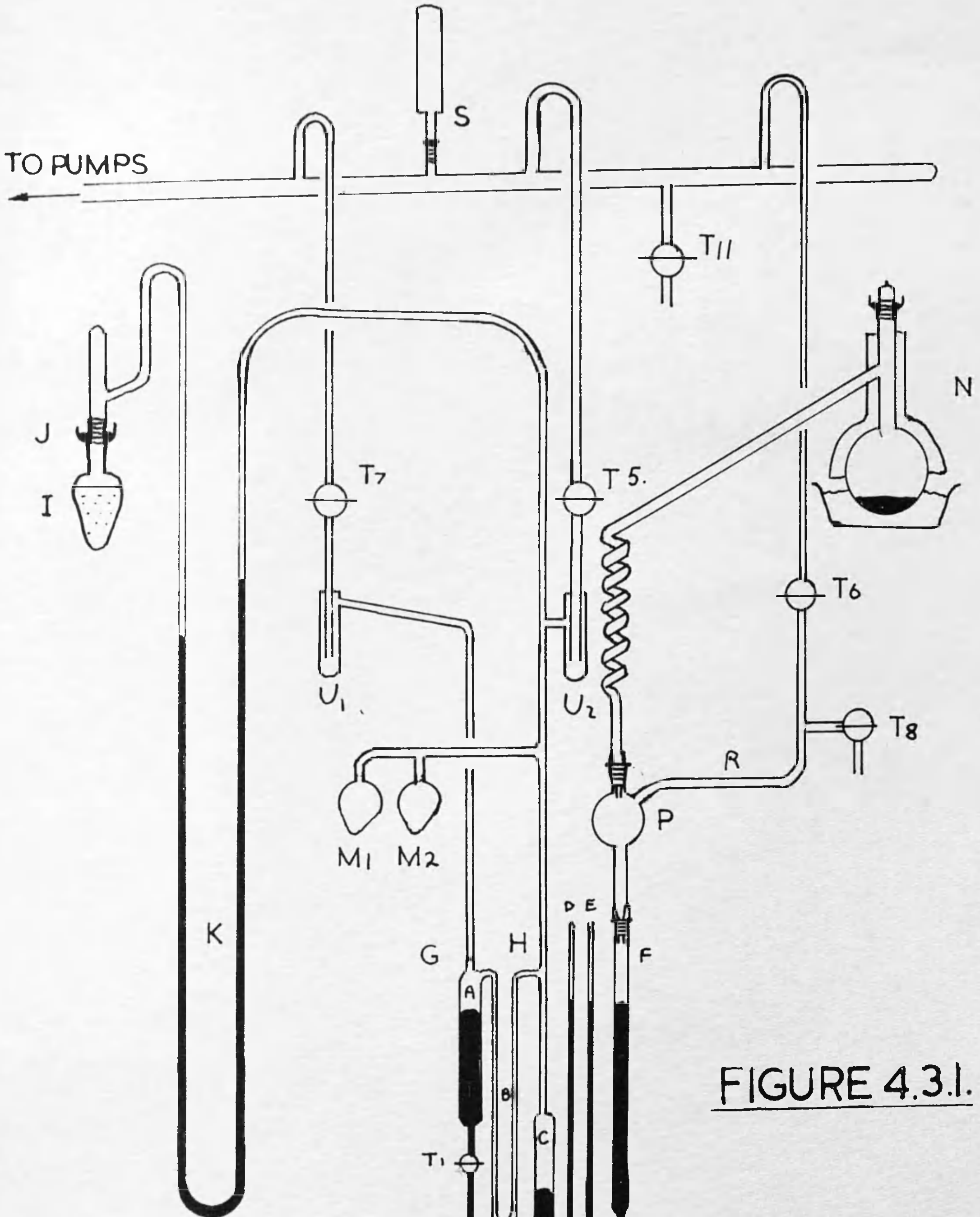


FIGURE 4.3.1.

THE VACUUM LINE.

The main degassing of the cyclohexane was carried out in the 100 cm^3 capacity pear-shaped flasks M_1 and M_2 before being distilled into the storage tube C of the dilatometer.

The dimer component was degassed in situ in the mixing tube A of the dilatometer, which was connected to the main vacuum line through tap T_7.

Small grease-traps U_1 and U_2 were inserted below stopcocks T_5 and T_7 to prevent grease, softened by hydrocarbon vapour, from reaching the pure components.

The mercury distillation unit comprised a magnesia-lagged distillation flask N to which a spiral, glass air-condenser was sealed. The distillation flask was stoppered by a mercury sealed B 29 joint and it was heated by a Meker burner. The distillation unit was joined to an intermediate vessel P through a greased B 14 joint and was evacuated through a tube leading from P to the main vacuum line through stopcock T_6. T_8 was an air inlet. The intermediate vessel P was attached to the B19 socket at the top of tube F of the dilatometer.

4.4. The Thermostat. When the dilatometer was fully charged it contained about 30 cm^3 of hydrocarbon liquid and a change in temperature of 0.01°C caused a displacement of the mercury in capillary D of 0.3 cm. It was thus necessary to place the dilatometer in an accurately controlled thermostat.

The thermostat consisted of a lagged steel tank containing water, the temperature of which was maintained by two electric heaters. One of the heaters was controlled by an electronic relay operated by a mercury-toluene regulator placed in the bath water.

The tank was made of galvanized steel and measured $1\frac{1}{2}$ ft X $\frac{3}{4}$ ft. in cross-section and was 2ft deep. Its capacity was 14 gallons. The largest pair of sides of the tank were fitted with rectangular observations windows of dimensions 12" X 14". One of these was made of armour-plate glass and the other of 3/8" thickness Perspex.

When the dilatometer was immersed in the bath, the taps T_1, T_2, T_3 and T_4 were operated from outside the bath by means of "hands" which were attached to ¼" diameter brass rods passing through flexible rubber bushes cemented into appropriately placed holes in the Perspex window. The "hands" were made of U-shaped channels of brass which engaged the crosspieces of the taps. Silicone grease was used to lubricate the brass rods and no trouble was experienced from sticking or leakage between the brass and the rubber. The outer ends of three of the rods were fitted with 2" diameter knobs. The rod operating tap T_3 was fitted with a 4" diameter knob to enable finer control to be obtained over the opening of this tap.

The water in the tank was treated with sodium nitrite and sodium benzoate to reduce corrosion.

The sides of the tank were lagged with fitted sections of resin bonded Fibreglass of thickness 1½". The bottom of the tank rested upon large cork rings placed on the base of the plywood box which enclosed the tank and insulation. Mineral wool was used to fill the spaces between the cork rings. The ends of the wooden box were hinged to allow access to the heater connections. Double doors were fitted to give access to the observation windows of the tank.

Heat losses caused by evaporation and radiation from the surface of the water were minimized by covering the top of the tank with 3/8" thickness "Sindanyo" sheet. This was fitted in a moveable and a fixed section. The fixed section was mounted on pads of sponge rubber plased on top of the tank. The stirring motors and a copper cooling coil were attached to this section. The moveable section was supported by two $\frac{1}{2}$" square steel bars which rested across the top edges of the sides of the wooden box enclosing the thermostat. The dilatometer was suspended from the moveable section when it was in use in the thermostat.

The water temperature was maintained using two electric immersion heaters, inserted centrally through opposite ends of the tank about 4" above the bottom. One heater was used to supply background heat and at a steady rate, so that when used alone, it produced a bath temperature two or three degrees below the desired temperature. Its rating was 2500 watts and its output was controlled by varying the input supply voltage using a Variac autotransformer. The other heater was used to obtain the desired temperature by operating in an on-off fashion under the control of the relay. Its rating was 250 watts and its output was also adjusted using a Variac autotransformer.

The main body of the mercury-toluene regulator was a three inch diameter helix, of total length one foot, made of 3/8 " outside diameter copper tubing. This was supported on three brass legs which rested on the bottom of the tank. Commercial copper glass seals were brazed on to both ends of the helix, lower one being sealed. The upper end was connected to the electrical contact mechanism through a double bend. The regulator contained 200 cm^3 of dry redistilled toluene which formed an interface with the mercury in the middle section of the double bend section. The mercury and copper thus were never allowed to come into contact.

The object of the design of the regulator was to provide a large surface-area to volume ratio in an attempt to diminish detector lag in the temperature control system. It was hoped that the high thermal conductivity of copper would assist in this, but the presence of a contaminant film on the surface of the copper probably cancelled any advantage which might have been obtained.

The mercury contact system was of the normal type, except that the mercury was earthed to the bath water by means of a platinum wire passing through the glass wall. The relay was sufficiently sensitive to operate on the small current which returned through the earthing system of the unit. The electronic relay was of conventional design and was built around a mercury contact switch which operated on a current of one milli-amp.

The following procedure was used to set the temperature of the bath. The water was heated using both heaters at full output until the temperature was within a few tenths of a degree of the desired temperature. The output of the background heater was then reduced to a value which was known previously to maintain the bath two or three degrees below this. The final heating to the exact temperature was carried out by the on-off heater. The tap on the regulator was then closed and fine adjustment was made by altering the position of the platinum contact wire in the capillary. The final adjustment was made by reducing the output of the on-off heater until its on-off periods were of roughly equal duration. These were generally two to three seconds.

The laboratory temperature commonly exceeded 20°C on warm days and so when working at 20°C, the bath water was cooled by passing cold tap water through a copper coil suspended from the fixed section of the Sindanyo cover. The rate of flow of cooling water was adjusted using a constant head device. A flow rate of 20 cms per minute was usually satisfactory.

The bath water was stirred by two stainless steel propeller-bladed stirrers mounted on vertical stainless steel shafts at each end of the bath about four inches above the heater elements. They were operated by Cintenco type stirring motors at 1500 r.p.m. mounted on the fixed section of the Sindanyo bath cover.

The temperature of the bath was measured using a set of N.P.L. calibrated thermometers. The set was manufactured by C.H. Zeal and Co. and comprised eleven mercury-in-glass thermometers covering the range -10°C to 100°C in steps of ten degrees each with graduations at 0.02°C intervals. These were used totally immersed in the bath and the temperature was read through the observation window using the cathetometer.

4.5. The Cathetometer. The mercury surface heights were measured using a cathetometer manufactured by the Precision Tool and Instrument Company. All measurements were made at room temperature and since the full precision obtainable with the cathetometer was not utilized, no compensation for temperature variations was made. The scale could be read to 0.001 cm. using the vernier and the small telescope provided.

4.6. The Dilatometer Support. The dilatometer was held in working position in the bath by means of a simple cradle suspended by steel rods from the moveable section of the tank cover.

The cradle consisted of a shaped piece of 3/8" thickness Sindanyo sheeting to which the dilatometer was clamped, and a footpiece of the same material on which the dilatometer rested, the footpiece being joined to the main section by two brass rods. Each end of the cradle was attached to a ½" diameter steel rod which passed through a brass boss on the moveable section of the bath cover. The height of the cradle in the bath could be altered simply by shifting the position of the clamps on the steel rods above the bosses, which prevented the rods from slipping through.

The moveable section of the lid rested on the exterior wooden box and thus the dilatometer was largely isolated from vibration from the stirring motors.

Chapter 5.

The Use of the Apparatus.

5.1. Introduction.

The present chapter is an account of the experimental technique which was followed in measuring excess volumes of mixing using the dilatometer and associated apparatus which have been described in the last chapter.

5.2. Charging the Dilatometer.

In order to eliminate traces of undissolved gas, which, due to the high compressibility of gases, could cause faulty measurements, the dimer component was thoroughly freed from dissolved gas in the dilatometer before use, and the mercury and cyclohexane were introduced by vacuum distillation.

Initially the dilatometer was fused to the vacuum line at G and H, the mercury distillation unit was assembled and greased B7 stoppers were fitted into the sockets on capillaries D and E. The apparatus was tested for vacuum-tightness and was then pumped out for at least one hour at a pressure of below 10^{-5} mm. Hg., all stopcocks T_1 to T_7 being open.

Mercury was then distilled into the dilatometer under vacuum. Stopcock T_3 was closed as soon as the mercury level rose above it and distillation was discontinued when the mixing vessel A was about two-thirds full of mercury. Stopcocks T_1, T_2, T_4 and T_6 were closed and the system, except for the mercury distillation unit, was restored to atmospheric pressure by admitting air through tap T_{11}.

The dimer component was introduced into the apparatus using a small, 6 cm^3. capacity, glass phial which was made from part of a 2 cm. diameter boiling tube. The phial was drawn out to form a long thin neck which was bent to form a right angle.

The phial was filled by heating the air in the body with the tip of the neck dipping below the surface of a quantity of the dimer contained in a clean weighing bottle. On cooling, a small quantity of liquid was drawn into the body of the phial. This liquid was boiled using a small gas flame, thus expelling most of the air from within the phial. When the phial was cooled, the dimer vapour condensed resulting in a partial vacuum which caused liquid to be drawn into the phial until it was nearly filled. The nearly full phial, suspended in a copper wire sling was then weighed.

The tube leading from tap T_7 to the mixing vessel A was cracked open about half an inch above the top of A and the upper portion was heated to softening point about six inches above the break so that it could be swung aside to expose the tube leading into A. The neck of the phial was then placed in the lower portion of the tube with the tip extending into A and about 3g. of the dimer were transferred directly into the dilatometer by heating the air in the body of the phial. The phial was allowed to cool in position and was then carefully removed and reweighed. The mass of dimer in the dilatometer was given by the difference between the two weighings.

The upper section of the vacuum-line connections was quickly replaced in its previous position and re-sealed to the dilatometer. The dimer in A was frozen using powdered drikold contained in a paper cone which was placed around A resting on a Terry clip. The fresh joint was tested for vacuum-tightness.

One of the dimer components, t-butylcyclohexane, does not freeze at the drikold temperature, $-78^\circ C$, but its vapour pressure at this temperature was estimated by extrapolation of boiling point data to be less than 10^{-3} mm.Hg. and it was assumed that a negligibly small quantity was lost by evaporation at $-78^\circ C$ during the pumping involved in the leak-testing and the subsequent degassing operations.

The dimer was freed from dissolved gas by the following procedure. The mixing vessel A, containing the frozen dimer at -78°C, was pumped out for about ten minutes at a pressure of less than 10^{-3} mm.Hg. through tap T_7. After closing T_7 and removing the drikold from around A, the dimer was melted using a stream of hot air from a hair-drier and was vigorously stirred with the magnetic stirrer to assist the passage of dissolved gas from the liquid into the vapour space. The dimer was then frozen again and the sequence of pumping, melting and re-freezing repeated until all visible traces of bubble formation on melting ceased. About six cycles of the degassing sequence were generally sufficient to achieve this.

Finally the dimer was frozen and the tube leading to tap T_7 was sealed off as close to the dilatometer as possible.

At the same time as the mixing tube A was being charged with the dimer component, tube C was being filled with cyclohexane. This was distilled from the reservoir I in two stages.

The storage tube C and the degassing flasks M_1 and M_2 were first pumped out and tap T_5 closed. The mercury in the U-tube K was lowered after the cyclohexane in I had been frozen using a drikold/CCl_4-CCl_3H cooling mixture. A Dewar vessel containing the same cooling mixture was placed around M_1 and the cyclohexane in I allowed to warm up and slowly distil into M_1. When approximately 80 cm^3. of cyclohexane were in M_1, the reservoir was isolated by raising the mercury in the U-tube K and the cyclohexane in M_1 subjected to the following degassing procedure.

The drikold cooling mixture around M_1 was replaced by a Dewar vessel containing liquid nitrogen. The system was then pumped out through tap T_5

for about a quarter of an hour at a pressure of less than 10^{-3} mm. Hg. On closing T_5 and replacing the Dewar flask with a beaker containing warm water, the cyclohexane melted. When all traces of solid had disappeared, the drikold mixture was replaced around M_1 and the cyclohexane was frozen again. The Dewar flask was then removed from M_1 and plesed around M_2 so that as the cyclohexane in M_1 warmed it slowly distilled from M_1 into M_2. When all the cyclohexane was transferred to M_2, the drikold cooling mixture was replaced with liquid nitrogen and the whole sequence was repeated. About four flask to flask distillations were generally found to be necessary to completely free the cyclohexane of dissolved gas. It may be noted that during the degassin operations, taps T_5 and T_7 were never open simultaneously, thus premature mixing of the dimer and cyclohexane was avoided.

The second stage of distillation was accomplished by condensing the cyclohexane in tube C using powdered drikold contained in a paper cone as a coolant. The paper cone was moved up the outside of tube C as the level of cyclohexane rose. In this way a solid mass of cyclohexane was formed, free from voids. When C was nearly full, The Dewar flask containing liquid nitrogen was replaced around the flask from which distillation was taking place, in order to solidify the excess cyclohexane.

Tap T_5 was then opened and while the pressure was maintained below 10^{-3}mm.Hg, the tube leading to T_5 was sealed off at H, just above the side arm to the U-tube B.

The excess cyclohexane in the degassing flask was returned to the reservoir by a distillation process identical to that by which it was withdrawn from I.

The pressure within the mercury still was then brought up to atmospheric pressure by admitting air through tap T_8 at the same time quickly removing the B7 stopper in capillary E, the B7 stopper in capillary D was removed immediately afterwards.

The tube between the intermediate vessel P and tap T_6 was cracked open at point R and the dilatometer freed from the vacuum line by first removing the mercury still and then the intermediate vessel P.

The dilatometer was removed from the environment of the vacuum line to be prepared for use.

The meniscus shield and the stirrer magnet were clipped into position around tubes C and A respectively and the removeable section of the bath cover was carefully fitted over the control rods for those fittings and over the steel rods of the cradle. The position of the cover was adjusted only roughly. The connections for the air reservoir were fitted into the B7 joints on capillaries D and E and were secured in place with springs. A long tube was fitted into the B19 socket on tube F, to prevent the bath water entering.

The dilatometer was then ready to be placed in the thermostat bath.

5.3. Equilibration and Preparation.

The dilatometer was placed in the thermostat bath and its position adjusted by shifting the clamps on the steel supporting rods of the cradle until all the taps were opposite the appropriate manipulating "hands" fixed in the windows of the tank. Slight out of alignment of tap and "hand" was unimportant since the rubber bushes allowed a certain degree of freedom of movement to the latter.

The progress of thermal equilibration of the liquids in the dilatometer was followed by watching the movement of the mercury in the U-tube B which acted as a rough manometer registering the vapour pressure of the cyclohexane in tube C. When the mercury level became stationary, as observed using the cathetometer, it was assumed that the dilatometer and its contents had reached the temperature of the thermostat. This occurred about thirty minutes after the dilatometer was first placed in the bath, a further thirty minutes was allowed to elapse before mixing operations were begun.

The first step towards the mixing process was the elimination of the vapour spaces above the liquids in tubes A and C. This was achieved by by opening taps T_1 and T_3 alternately thus admitting mercury from the reservoir tube F into the tubes A and C and diminishing the vapour spaces. When C was nearly full of liquid, the rate of admission of mercury through tap T_3 was greatly reduced so that when all the vapour space above the cyclohexane disappeared, liquid slowly entered the U-tube B and displaced the mercury into A. Meanwhile the vapour space in A was reduced to a small amount at the top of the tube and tap T_1 was closed.

Great care was required while the mercury in the U-tube was being displaced, because, as the cyclohexane was rising in the left hand limb, a point was reached where the length of the mercury column above the cyclohexane became insufficient to balance the vapour pressure of the cyclohexane which then began to vapourize at the top of the tube leading up from tube C. This caused the cyclohexane in the U-tube to be rapidly forced out into tube A where premature mixing took place. This premature mixing could be avoided by admitting the mercury into tube C sufficiently slowly that the onset of rapid movement could be readily detected whereupon tap T_3 was closed and T_1 quickly opened. The effect of this action was to fill the dilatometer with liquid completely, leaving only a small bead of mercury at the top of the left hand limb of the U-tube separating the two components.

In the cases where a small amount of premature mixing did occur, a graphical method, which will be described later, was used to correct its effect on the observed volume changes.

The final step before the first mixing was carried out was the addition or removal of mercury from reservoir F, until the mercury surface in F was level with that in A. The hydrostatic pressure exerted on the organic liquids was then equal to atmospheric pressure. Tap T_4 was closed and the dilatometer was then ready for the first measurements.

5.4. Experimental Measurements and Mixing Technique.

Before commencing mixing, the original positions of the mercury surfaces in tube C and capillary D were measured. Since all subsequent measurements were referred to these, the initial measurements were the mean of five successive readings.

In spite of all precautions taken to avoid vibration of the dilatometer, the surface of the mercury in the wide tube C displayed considerable vibration. Therefore the stirring motors were switched off momentarily when the final adjustment of the telescope crosswires was being made.

After the preliminary measurements, the first displacement of cyclohexane was made. It was desired to make measurements of v^e at intervals of roughly 0.1 mole fraction and thus the displacements of cyclohexane had to be made systematically. The following formula was used to calculate the net displacement, Δl_c, of the mercury level in tube C from its initial position, which would produce a solution of the desired mole fraction in the mixing vessel A,

$$\Delta l_c = \left[\frac{M_1 \cdot (1 - x_2)}{x_2 \cdot A d_1^c} \right] n_2 \qquad 5.4.1.$$

where n_2 is the number of moles of the dimer component obtained from the known mass in the dilatometer, x_2 is its mole fraction in the solution, M_1 is the molecular weight of cyclohexane, d_4^t is its density at the temperature of the experiment t, and A is the cross-sectional area of tube C. Tables of the function within the square bracket were made up at intervals of 0.05 mole fraction for the different temperatures at which measurements were taken, thus facilitating the calculations of Δl_G.

The displacements were made by setting the cross-wire to the height calculated for a given displacement and opening tap T_3 slightly until the mercury rose in tube C to appear to touch the cross-wire. T_3 was then closed and the solution stirred vigorously. When the mixture reached equilibrium, as shown by the coming to rest of the mercury level in the capillary D, the following series of measurements was taken.

1. The level of the mercury in C, l_G, was measured first, since this was unaffected by the state of equilibrium in tube A.

2. The level of a hair scratch on tube C was measured, l_{ref}. Changes in this during an experiment indicated whether the apparatus moved during any given mixing process. If a change of position was found, an appropriate correction was made to l_G and the final measurement of the meniscus level in capillary D, l_D.

3. The levels of the mercury in tubes A, D and F were measured to ± 0.01cm so that the position of the mercury level in capillary E, l_E, could be calculated as described previously. l_E was calculated from the equation,

$$l_E = l_F - (l_A - l_D) \qquad 5.4.2.$$

In practice l_F did not vary during the course of an experiment within the accuracy of the measurement and only l_A and l_D were measured each time.

The cross-wire was set to the required position and the mercury level in capillary E was adjusted to this by adding or removing air from the reservoir flask. The final adjustment was always made using a rising meniscus in order to minimize surface tension errors in the narrow capillary.

Further checking of the levels ℓ_A and ℓ_D after the level of the mercury in E was fixed was found to be unnecessary since it was found by direct measurement that the change in position of D caused by a further balancing procedure was generally within the experimental accuracy of the setting procedure.

4. The final measurement was that of the mercury level in capillary D after the pressure balancing operations.

5. The position of the cross-wire was now set for the next displacement in tube C and the sequence of measurement repeated.

The secuence of mixing and taking measurements was usually repeated at least nine times to cover the composition range adequately. Towards the end of an experiment, when the volume of liquid in A was fairly large, additional time was recuired before equilibrium was re-established after the addition of more cyclohexane.

In cases where it was thought that v^e would be large, additional mixings at intermediate mole fractions were made to establish the position of the minimum in the curve.

At the end of the experiment, the dilatometer was removed from the bath and clamped in a fixed position. The fittings were all removed, i.e. meniscus shield, stirrer magnet, air reservoir connections etc. and the mercury sucked out of F using a long thin polythene tube. The bulk of the liquid in the dilatometer was transferred into tube F by evacuating this tube with stoppers in capillaries D and E and tap T_4 open. This liquid was removed after closing tap T_4 and restoring atmospheric pressure. Repetition of this process allowed most of the liquid to be recovered in an uncontaminated form. The mercury and the hydrocarbon liquids were separated, the former being returned to the mercury still and the latter put aside for recovery and re-purification of the dimer component.

The dilatometer was evacuated using a rotary oil pump alone for about an hour to remove all the volatile remnants of the liquids. The apparatus was opened for more thorough cleaning by heating the seals on tubes A and C and blowing them open. Fresh pieces of tubing were sealed to the dilatometer in preparation for its being joined to the vacuum line for the next experiment.

The apparatus was cleaned by successive washings with acetone and distilled water. The taps and greased joints were cleaned using low boiling petroleum ether. The dilatometer was then filled with fresh chromic acid cleaning mixture and was laid aside in this condition for at least twenty-four hours. The final traces of chromic acid were then removed by several washings with distilled water after which the whole dilatometer was placed in an air oven at 120°C for an hour to remove final traces of water, all the keys being removed from the taps.

The dilatometer was then sealed to the vacuum line as before, in readiness for the next experiment.

Addendum to Section 2.

It was later found that the freezing-point of t-butylcyclohexane is -41°C. The only explanation for the apparent non-freezing of this substance when being degassed at -78°C, is that the mercury in the tube provides a sufficiently large heat source that the actual temperature of the liquid never drops below -40°C.

Chapter 6.

The Preparation of Materials.

6.1. Introduction.

This chapter contains descriptions of the methods which were used to obtain pure samples of the materials which were studied.

Several of the desired compounds were obtained from the corresponding aromatic compounds by catalytic hydrogenation which was carried out under high pressure in an autoclave using cyclohexane as solvent. The catalyst was Nicat catalyst, manufactured by J. Crosfield and Co. Ltd. Nicat catalyst is composed of finely divided nickel supported on a silica substrate. It is similar to Raney nickel in catalytic activity, but has the advantage that it is non-pyrophoric and is obtained ready for use without pre-activation.

All the dimer compounds were freed from traces of aromatic impurities by passage, in pure cyclohexane solution, through silica gel.[80, 81.] The silica gel was Hopkins and Williams M.F.C. grade.

Freezing-point time-temperature curves were obtained using an apparatus similar to that described by Glasgow, Streiff and Rossini.[82] The liquid was stirred mechanically and its temperature was measured using a Stantel F22 type thermistor, the resistance of which was determined using a Wheatstone bridge network incorporating fixed and variable standard resistances. The thermistor, which had a resistance at 0°C of 441ohms and a temperature coefficient of the logarithm of resistance of 0.0152 deg.^{-1}, was calibrated between -10°C and 20°C by comparison with the N.P.L. calibrated thermometers, and below -10°C by a determination of the freezing-point of distilled mercury.

The purity of each sample was calculated from the freezing-point time-temperatures curves. When a reliable value for the freezing-point t_{fo}

of the pure substance was available, the purity was calculated from the simple equation,

$$1 - x_1 = \frac{-(\Delta H_{fo})(\Delta T_{fo})}{R T_{fo}^2} \qquad 6.\ 1.\ 1.$$

where x_1 is the mole fraction purity of the material, $-\Delta H_{fo}$ is the molar latent heat of crystallization and T_f and T_{fo} are the freezing-points of the sample and the pure material. The procedures described by Taylor and Rossini,[83] and Guggenheim and Prue[84] were used in cases where T_{fo} was not known exactly.

Vapour phase chromatography was also used to confirm the purity of the samples. The apparatus used was a Griffin V.P.C. apparatus Mk.11.b., employing columns of silicone oil on Celite.

The infra-red spectrum of each compound was determined in order to detect traces of aromatic impurities. These were recorded on a Grubb-Parsons double-beam recording spectrophotometer.

The density determinations were carried out using modified Sprengel type pyknometers.[85] This set of measurements will be described in more detail in chapter eight.

The ultra-violet spectrum of cyclohexane was recorded on a Hilger S.P.500 spectrophotometer. The refractive indices were measured using an Abbé refractomete

All materials were stored over sodium in conical flasks, the ground-glass stoppers of which were fitted with Teflon sleeves.

6.2. Cyclohexane.

'Spectrosol' grade cyclohexane, supplied by Hopkins and Williams, was considered to be free from aromatic impurity on the basis of the ultra-violet spectrum of a representative sample. This spectrum was compared, under similar conditions, with the spectrum of a sample of cyclohexane which had been specially treated to remove aromatic impurities.[86] The two spectra were identical.

The cyclohexane was fractionally distilled from sodium, using a fractionating apparatus manufactured by Griffin and George Ltd. The column was packed with stainless steel Dixon gauze rings and was stated to have an efficiency of around forty theoretical plates. The fractionations were conducted using 2000 cm^3 batches of cyclohexane, of which the middle fraction of 1500 cm^3 was retained for subsequent purification by repeated fractional crystallization.

The vapour phase chromatogram of the pure, dry material showed only one peak and the purity was found to be 99.61% mole fraction. The physical properties of the cyclohexane are given in table 6.2.

6.3. t-Butylcyclohexane.

t-Butylcyclohexane was obtained by catalytic hydrogenation of t-butylbenzene. The latter material, supplied by L. Light and Co. Ltd. was redistilled before conversion. The conditions of the hydrogenation were 230°C and 100 atmospheres pressure of hydrogen.

The product, after passage through a column packed with silica gel, was fractionally distilled under reduced pressure using a short column packed with glass beads. The identity of the product was confirmed by its refractive index, density, infra-red spectrum and carbon-hydrogen analysis. The details of the measured physical properties are given in table 6.3. The quoted value of the freezing-point is only approximate due to the necessity to extrapolate the calibration of the thermistor over a wide range of temperature. The purity could not be calculated readily for the same reason but the comparison of the values of the observed physical properties with those obtained from literature sources suggest that the material was sufficiently pure for the measurements envisaged.

6.4. Dicyclohexyl.

Commercial grade dicyclohexyl was obtained from L. Light and Co. Ltd. and was subjected to a preliminary distillation before being purified in a similar manner to that used for t-butylcyclohexane. The purity was found to be 99.98 %.

An attempt was made to purify dicyclohexyl by zone-refining using the technique described by Röck,[87] for benzene. This attempt was unsuccessful principally due to the cracking, during the melting process, of the glass annular vessel used to contain the dicyclohexyl. Purification using the growing of a single-crystal[88] also proved unsuccessful. This was considered to be due to a transition point in the solid between its freezing-point and the temperature of the cooling mixture, -78°C.

The physical properties of the dry, pure product are given in table 6.4.

6.5. Dicyclohexylmethane.

Dicyclohexylmethane was prepared by the catalytic hydrogenation of diphenylmethane which was obtained from L. Light and Co. Ltd. The aromatic hydrocarbon was distilled under reduced pressure before conversion. The hydrogenation was carried out at 220°C and 40 atmospheres pressure. The product was purified in a similar manner to that of t-butylcyclohexane. The purity was found to be 98.3 %.

The identity of the product was confirmed by its refractive index, density, infra-red spectrum and carbon-hydrogen analysis.

The physical properties of dicyclohexylmethane are given in table 6.5.

6.6. 1,2-Dicyclohexylethane.

1,2-Dicyclohexylethane was obtained by catalytic hydrogenation of 1,2-diphenylethane which was supplied by L. Light and Co. Ltd. The latter compound was recrystallized from cyclohexane befor hydrogenation. The temperature and pressure of hydrogenation were 220°C and 70 atmospheres. The purification was carried out as for t-butylcyclohexane. The purity was 97.5 %.

The identity of the product was confirmed from its refractive index, density, infra-red spectrum and carbon-hydrogen analysis. The physical properties of 1,2-dicyclohexylethane are given in table 6.6.

6.7. 1,3-Dicyclohexylpropane.

Dibenzyl ketone, supplied by Hopkins and Williams, was reduced to 1,3-diphenylpropane using the Huang-Minlon variation [37] of the Wolff-Kishner reduction. This involved the formation of dibenzyl ketone hydrazone and its subsequent breakdown ~~hydrolysis~~ by sodium hydroxide in diethylene glycol solution. The identity of the 1,3-diphenylpropane was confirmed from its infra-red spectrum and by its boiling-point. A check on its purity was made using vapour phase chromatography.

1,3-Dicyclohexylpropane was obtained by catalytic hydrogenation of 1,3-diphenylpropane at 230°C and 100atmospheres. The reaction was difficult to initiate and the catalyst had to be pre-activated by treatment, in the solid state, with hydrogen at 400°C in a furnace.

The 1,3-dicyclohexylpropane was purified in a similar manner to t-butylcyclohexane. The purity of the final product was 97.8%and its identity was confirmed by its density and freezing-point. The physical properties of 1,3-dicyclohexylpropane are given in table 6.7.

Table 6.2.

The Physical Properties of Cyclohexane.

Formula C_6H_{12}. Molecular Weight 84.15_6.

Freezing-point.	5.55°C.	This Work.
	6.55°C.	Swinton.[90]
	6.541°C.	Forziati et al.[91]
	6.554°C.	Bureau of Standards Tables.[92]
Density. d_4^{25}	0.7737_5 $g.cm^{-3}$.	This Work.
	0.7739_0 "	Swinton.[90]
	0.7738_3 "	Scatchard et al.[93]
	0.7738_9 "	Bureau of Standards Tables.[92]
	0.7738_4 "	Rotinjanz et al.[94]
Latent Heat of Fusion.		
	624 $cal.mole^{-1}$.	Glasstone.[95]
Purity Factor.		
	$0.0041 deg^{-1}$.	

Table 6.3.

The Physical Properties of t-Butylcyclohexane.

Formula $C_{10}H_{20}$. Molecular Weight 140.26_0.

Boiling-point.	170°C / 760mm.Hg.		This Work.
	168.2°C / 760mm.Hg.		Baker et al.[96]
Freezing-point.	-37.5°C.		This Work.
	-41.158°C.		Streiff.[98]
Density. d_4^{20}	0.8102	g.cm^{-3}.	This Work. (extrapolated value).
	0.811	"	Ward et al.[97]
Refractive Index.			
	1.4511	n_D^{17}	This Work.
	1.4535	n_D^{11}	Stratford.[100]
	1.4468	n_D^{20}	Baker et al.[96]
	1.4464	n_D^{20}	Ward et al.[97]
	1.4482	n_D^{20}	Herington.[101]
	1.4469_4	n_D^{20}	Fortziati.[99]
Purity Factor.	0.0303deg^{-1}.[98]		

Table 6.4.

The Physical Properties of Dicyclohexyl.

Formula = $C_{12}H_{22}$. Molecular Weight = 166.29$_6$.

Boiling-point.	237°C /760m.m.Hg.	This Work.
	233–234°C /760m.m.Hg.	Sabatier et al.[102]
	239.5–240°C/760m.m.Hg.	Zelinsky et al.[103]
	237–238.5°C/757m.m.Hg.	Ipatieff et al.[104]
	233°C /760m.m.Hg.	Hückel. et al.[105]
	236.8°C /760m.m.Hg.	Venus-Danilowa.[106]
Freezing-point.	3.88°C	This Work.
	2.86°C	Swinton.[90]
	2.25°C	Hückel et al.[105]
	2.75°C	Mascarelli etal.[107]
	3.6 °C	Chemikers Handbuch.[108]
Density.	0.8859 g.cm^{-3}.	This Work (extrapolated value).
	0.8871$_5$ g.cm^{-3}.	Swinton[90] (interpolated value).
	0.8846 g.cm^{-3}.	Egloff.[109]
Refractive Index.	n_D^{20}	
	1.4838 n_D^{17}	This Work.
	1.4800 n_D^{20}	Zelinsky et al.[103]
Latent Heat of Fusion.		
	1744cal., mole.$^{-1}$	Mascarelli et al.[107]
Purity Factor.		
	0.0114deg.$^{-1}$	

Table 6.5.

The Physical Properties of Dicyclohexylmethane.

Formula = $C_{13}H_{24}$. Molecular Weight = 180.32_2.

Boiling-point.	251°C/760m.m.Hg.	This Work.
	252.8°C/760m.m.Hg.	Serijan and Wise.[110]
	110-110.5°C/18m.m.Hg.	Adams and Marshall.[111]
	250-252°C/760m.m.Hg.	Zelinsky et al.[103]
Freezing-point.	-20.46°C.	This Work.
	-18.70°C.	Serijan and Wise.[110]
Density. d^{20}_{4}	0.8776_9 g.cm^{-3}.	This Work.
	0.8764_6 "	Serijan and Wise.[110]
	0.8884 "	Adams and Marshall.[111]
	0.8725 "	Ipatieff et al.(1). (d^{20}_{0}).[104]
	0.8743 "	Ipatieff et al.(2). (d^{20}_{0}).[112]
	0.8750 "	Zelinsky et al.[103]
Refractive Index.		
	1.4790 n^{17}_{D}	This Work.
	1.4755 n^{21}_{D}	Ipatieff.[104]
	1.4763 n^{20}_{D}	Serijan and Wise.[110]
Latent Heat of Fusion.		
	4100 cal.mole^{-1}.	Serijan and Wise.[110]
Purity Factor.		
	0.032deg.$^{-1}$	

Table 6.6.

The Physical Properties of 1,2-Dicyclohexylethane.

Formula $C_{14}H_{26}$. Molecular Weight 194.34_8.

Boiling-point.		136.8°C / 15mm.Hg.	This Work.
		136°C / 15mm.Hg.	Venus-Danilowa.[106]
		274.0°C / 760mm.Hg.	Serijan and Wise.[110]
Freezing-point.		7.85°C.	This Work.
		11.45°C.	Serijan and Wise.[110]
Density.	d_4^{20}	0.8772_0 $g.cm^{-3}$.	This Work. (extrapolated value).
	d_4^{20}	0.8739_5 "	Serijan and Wise.[110]
	d^{24}	0.8778 "	Zelinsky et al.[103]
	d^{18}	0.8774 "	Adams and Marshall.[111]
Refractive Index.			
		1.4830 n_D^{17}	This Work.
		1.4760 n_D^{18}	Adams and Marshall.[111]
		1.4759 n_D^{20}	Serijan and Wise.[110]
Latent Heat of Fusion.			
		6300 $cal.mole^{-1}$.	Serijan and Wise.[110]
Purity Factor.			
		$0.039 deg^{-1}$.	

Table 6.7.

The Physical Properties of 1,3-Dicyclohexylpropane.

Formula $C_{15}H_{28}$. Molecular Weight 208.37_4.

Freezing-point.	-15.38°C.	This Work.
	-14.82°C.	Serijan and Wise.
Density. d_4^{20}	0.8723_7 g.cm^{-3}.	This Work.
	0.8712_8 "	Serijan and Wise.
Refractive Index.		
	1.4780 n_D^{17}	This Work.
	1.4752 n_D^{20}	Serijan and Wise.
Latent Heat of Fusion.		
	6200 cal.mole^{-1}.	Serijan and Wise.
Purity Factor.		
	0.047deg^{-1}.	

Chapter 7.

Experimental Results.

7.1. Introduction.

In this chapter, an account is given of the procedure followed in order to calculate from the observed readings, the composition of the solution being studied at a given stage in the experiment and the corresponding value of the excess volume of mixing. The method of correcting the observed volume changes in the systems to allow for small amounts of premature mixing is also described. Component 1 in all cases is cyclohexane and component 2 is the dimer compound e.g. dicyclohexylmethane.

7.2. Calculation.

The composition of the solution, x_2, at a given stage during an experiment was calculated using the following equation,

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{m_2}{M_2}}{\frac{m_2}{M_2} + \Delta l_c\left(\frac{A_c d^t_{4,1}}{M_1}\right)} \qquad 7.\ 2.\ 1.$$

In this equation, n_1 and n_2 are the number of moles of components 1 and 2 in the mixing vessel A, M_1 and M_2 are the molecular weights of the components, m_2 is the mass of component 2, A_c is the cross-sectional area of tube C, $d^t_{4_1}$ is the density of component 1 at the temperature of the experiment, t, and Δl_c is the linear displacement of the mercury in tube C after correction for bulk movement of the dilatometer during the manipulations.

The quantity $\frac{A_c d^t_{4_1}}{M_1}$ was calculated for each temperature and used as a factor for Δl_c to obtain n_1.

Tube C was made from Veridia tubing. Its internal diameter was 1.500 ± 0.001cm. and its cross-sectional area was 1.767 ± 0.003cm^3. The increase in the cross-sectional area on heating from 20°C to 40°C was 0.00021cm^2. This small change was negligible and the cross-sectional area was taken as constant over the range of temperature covered.

The actual volume change, ΔV, which occurred in the system was calculated from the equation,

$$\Delta V = A_E \cdot \Delta l_E. \qquad 7.\ 2.\ 2.$$

A_E is the cross-sectional area of capillary E and Δl_E is the net linear displacement of the mercury level in capillary E. This was made from Veridia capillary and the nominal internal diameter was 0.040 ± 0.001cm. The latter was checked in the manner described previously, and was found to be 0.04004 ± 0.00060cm. The cross-sectional area A_E was taken as 0.00126 ± 0.00004cm^2. The effect of temperature changes on A_E was negligibly small.

The excess volume of mixing could be calculated using the equation,

$$v^e = \frac{\Delta V}{n_1 + n_2} \qquad 7.\ 2.\ 3.$$

In practice, v^e was not calculated in this way. The quantity ΔV^*, defined by,

$$\Delta V^* = \frac{A_E . \Delta l_E}{n_2} \quad \frac{\Delta V}{n_2} \qquad 7.\ 2.\ 4.$$

was required in the calculations for the detection and correction of the small unmeasured volume changes which were caused by premature mixing, and the excess volume of mixing was calculated from this using the relationship,

$$v^e = \frac{\Delta V}{n_1 + n_2} = \left(\frac{\Delta V}{n_2}\right)\left(\frac{n_2}{n_1 + n_2}\right) = \Delta V^* . x_2. \qquad 7.\ 2.\ 5.$$

7.3. The Correction for Premature Mixing.

It was noted in chapter five that, during the first mixing in the dilatometer, a small amount of premature mixing occasionally took place which made impossible the precise measurement of the initial level of the mercury surface in capillary D. The following procedure was devised to permit the detection of such pre-mixing, and to evaluate the required correction terms.

The essence of the method was that, since the composition of the solution in the mixing vessel was known to a fair degree of accuracy throughout the experiment, a graphical plot of the values of Δl_g against the composition x_2 could be extrapolated to $x_2 = 1$, and an estimate made of the true, initial mercury level in the capillary E.

The justification for assuming that the composition of the mixture in A was known accurately throughout the course of the experiment, lies in the fact that the quantity of cyclohexane which caused the premature mixing was fairly small, of the order 0.01cm^3., and thus the measured initial position of the mercury surface in tube C was little different from the true initial position. The total cuantity of cyclohexane in the mixing vessel was therefore known precisely at all times, and as a consecuence, so also was the composition of the solution. The effect of premixing was to cause some uncertainty in the measured values of Δl_g and very slight uncertainty in the values of Δl_c.

The graphical correction plot used was not l_g v. x_2, but ΔV^* v. x_2. Since ΔV^* and Δl_g are proportional to one another, this change does not affect the final result but the use of ΔV^* has certain advantages.

In the first place, the number of moles of the dimer compound varied from experiment to experiment as a result of the differing masses and molecular weights. It was thus useful to normalize the volume changes to a common basis, namely the volume changes at given compositions for one mole of the dimer component.

Secondly, the plot allowed a quick evaluation of the value of v^e at $x_1 = x_2 = 0.5$. This followed from equation 7.2.5. from which it is clear that at $x_1 = x_2 = 0.5$,

$$v^e = 0.5\,\Delta V^* \qquad 7.3.1.$$

The normal procedure was that ΔV^* was calculated for each composition and a plot of ΔV^* v. x_2 was drawn on a large scale. The points usually fell on a smooth curve which could be readily extrapolated to $x_2 = 1$. In cases where no premixing took place, the curve passed through the origin and v^e was calculated directly from equation 7.2.5. In other cases, when a small amount of premixing did take place, the curve did not pass through the origin and the values of ΔV^* were then corrected by the addition or subtraction of an appropriate amount which corresponded to the volume change which had taken place before the first measurement of the mercury level in capillary E had been made. The corrected value of ΔV^*, termed ΔV^*_{corr}, was then used to calculate v^e.

Tables 7.3.1. and 7.3.2. contain specimen calculations for cases where premixing was absent and present respectively. Figures 7.3.1. and 7.3.2. show the corresponding correction plots and Figures 7.3.3. and 7.3.4. show the derived excess volumes of mixing.

7.4. Results.

The excess volumes of mixing of the following systems were studied at the stated temperatures.

1. Cyclohexane + t-butylcyclohexane, 20°C and 40°C.
2. Cyclohexane + dicyclohexyl, 20°C, 30°C and 40°C.
3. Cyclohexane + dicyclohexylmethane 20°C and 40°C.
4. Cyclohexane + 1,2-dicyclohexylethane 20°C and 40°C.
5. Cyclohexane + 1,3-dicyclohexylpropane, 20°C and 40°C.

The results of the measurements and the calculated values of v^e and x_2 are given in Tables 7.4.1. to 7.4.11. The following information is given in the tables of results,

TABLE 7.3.1.

Cyclohexane + 1,3-Dicyclohexylpropane. 20.00°C.

Mass DCHP = 3.39087 g. Moles DCHP (n_2) = $16.27_3 \times 10^{-3}$. Correction to ΔV^* = 0.000 cm³ mole^{-1}.

Δl_c cm.	n_1 moles X 10^3	$n_1 + n_2$ moles X 10^3	x_2	$-\Delta l_E$ cm.	$-\Delta V$ cm^3. X 10^3	$-\Delta V^*$ cm^3. mole^{-1}	$-V^E$ cm^3. mole^{-1}
0.118	1.93	18.20	0.8941	0.128	0.161	0.0099	0.00885
0.25	4.09	20.36	0.7991	0.483	0.607	0.0373	0.02981
0.51	8.49	24.76	0.6571	0.984	1.237	0.0760	0.04994
0.66	10.84	27.11	0.6003	1.275	1.603	0.0985	0.05913
0.91	14.91	31.18	0.5218	1.838	2.310	0.1420	0.07410
1.16	19.11	35.38	0.4599	2.425	3.048	0.1873	0.08614
1.71	28.04	44.31	0.3672	3.450	4.337	0.2665	0.09786
2.31	37.82	54.09	0.3008	4.097	5.150	0.3165	0.09520
3.89	63.60	79.87	0.2037	6.005	7.548	0.4638	0.09448

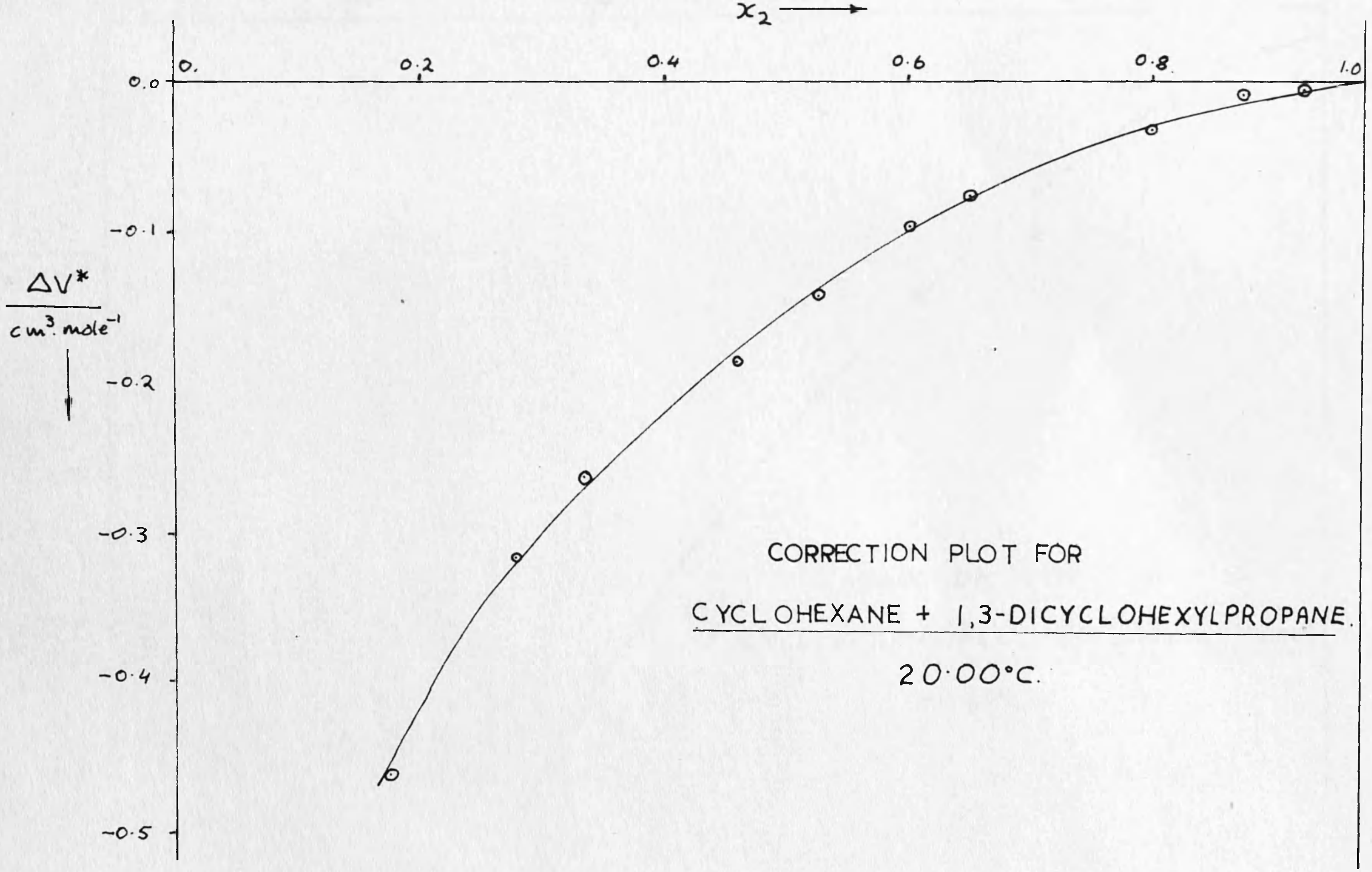
TABLE 7.3.2.

Cyclohexane + 1,2-Dicyclohexylethane. 40.21°C.

Mass DCHE = 2.9980$_8$ g. Moles DCHE (n_2) = 15.42$_6$ X 10^{-3}. Corr^n to $-\Delta V^*$ = -0.025 cm^3. mole^{-1}.

Δl_e cm.	n_1 moles X 10^3	$n_1 + n_2$ moles X 10^3	x_2	$-\Delta l_\varepsilon$ cm.	$-\Delta V$ cm^3 X 10^3	$-\Delta V^*$ cm^3. mole^{-1}.	$-\Delta V^*$ corr.	$-v^e$ corr. cm^3. mole^{-1}.	$-v^e$ uncorr.
0.070	1.12	16.55	0.9325	0.682	0.857	0.0556	0.031	0.029	0.0518
0.124	1.98	17.41	0.8863	1.057	1.329	0.0861	0.061	0.054	0.0763
0.225	3.59	19.02	0.8112	1.570	1.974	0.1279	0.103	0.0836	0.1038
0.370	5.11	20.54	0.7513	2.101	2.641	0.1712	0.146	0.1097	0.1286
0.472	7.53	22.96	0.6721	2.557	3.214	0.2083	0.183	0.1299	0.1400
0.697	11.12	26.55	0.5811	3.346	4.206	0.2727	0.248	0.1441	0.1584
0.989	15.75	31.18	0.4948	4.432	5.571	0.3611	0.336	0.1663	0.1787
1.437	22.93	38.36	0.4022	5.568	6.999	0.4537	0.429	0.1725	0.1825
2.233	35.63	51.06	0.3022	7.099	8.973	0.5817	0.557	0.1683	0.1757
3.681	58.73	74.16	0.2081	8.912	11.202	0.7262	0.701	0.1459	0.1511
8.339	133.05	148.78	0.1039	11.657	14.653	0.9500	0.925	0.0961	0.0965

FIGURE 7.3.1.

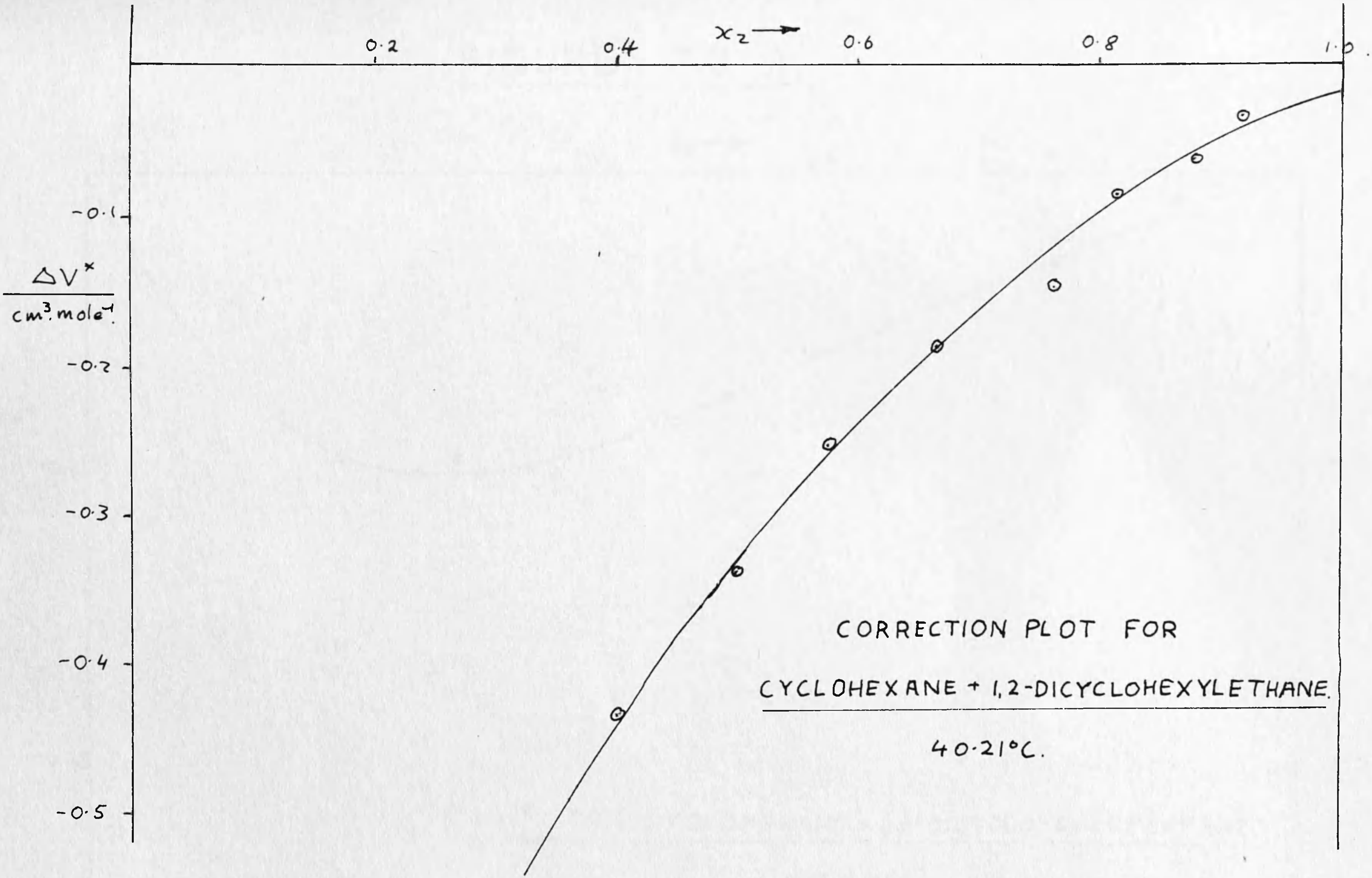


CORRECTION PLOT FOR

CYCLOHEXANE + 1,3-DICYCLOHEXYLPROPANE.

20·00°C.

FIGURE 7.3.2.

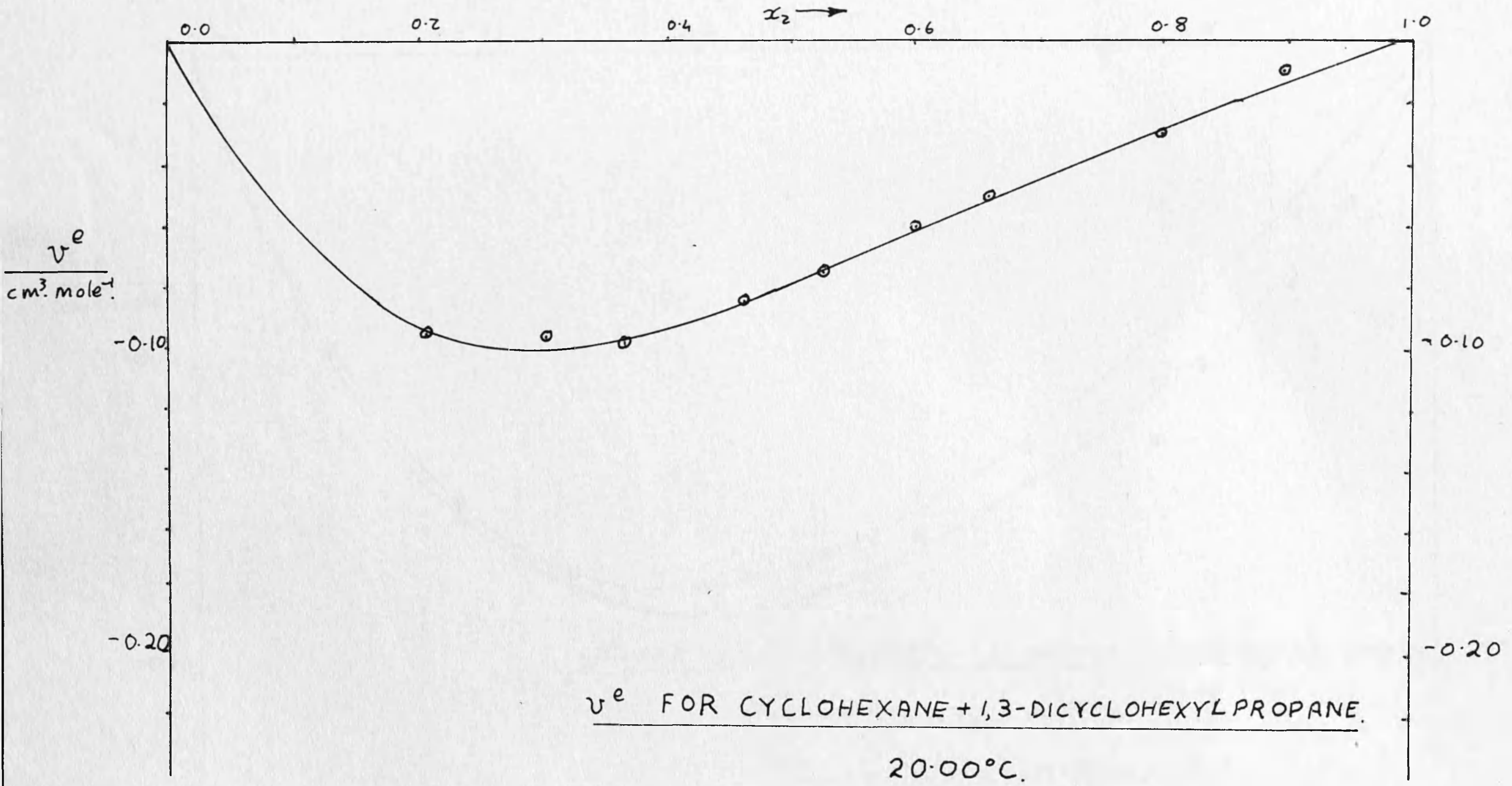


CORRECTION PLOT FOR

CYCLOHEXANE + 1,2-DICYCLOHEXYLETHANE.

40·21°C.

FIGURE 7.3.3.



v^e FOR CYCLOHEXANE + 1,3-DICYCLOHEXYL PROPANE.

20·00°C.

1. Δl_c – The net linear displacement of the mercury level in tube C, corrected for dilatometer movement.

2. x_2 – The mole fraction of component 2.

3. Δl_E – The net linear displacement of the mercury level in capillary E corrected for the dilatometer movement.

4. $\Delta V^{*}_{corr.}$ The corrected values of the net volume change in the system, normalized with respect to n_2.

5. v^e – The excess volume of mixing.

6. Δv – The percentage excess volume of mixing, calculated from the equation,

$$\Delta v = 100\left(\frac{v^e}{x_1v_1 + x_2v_2}\right) \qquad 7.4.1.$$

Also given for each series of measurements are the temperature of the experiment, the mass and number of moles of component 2, and the value of the correction term for premature mixing.

The results are also given graphically. Figures 7.4.1. to 7.4.5. show the values of v^e found at different temperatures plotted against x_2. Smooth curves are drawn through the points.

Mean values of $\frac{dv^e}{dT}$ between 20°C and 40°C at rounded mole fractions were calculated from the graphs using the relationship,

$$\frac{dv^e}{dT} = \frac{v^e_{40} - v^e_{20}}{40 - 20} \qquad 7.4.2.$$

These values are quoted for the different systems in Tables 7.4.12. to 7.4.16. and are shown in Figures 7.4.6. to 7.4.10.

7.5. The Limits of Accuracy of the Results.

The limits of accuracy in the quoted values of x_2 and v^e are discussed separately.

1. Errors in x_2.

(a). m_2. The mass of component 2, which was usually in the range 2.5 to 3.3g.

was measured to ± 0.00005g. which corresponds to an error of approximately ± 0.002%.

(b). d_4^t. The densities of cyclohexane were taken from the A.P.I. tables,[113] and were known to ± 0.0001g.cm.$^{-3}$ The uncertainty is approximately ± 0.012%.

(c). A_c. The diameter of tube C was taken, without checking, to follow the manufacturer's specification, i.e. 1.500 ± 0.001 cm. The cross-sectional area was 1.767 ± 0.003cm.^{3} and the uncertainty was approximately ± 0.12%.

(d). Δl_c. The uncertainty in Δl_c arose for two sources, the error in measuring the positions of the mercury meniscus and the error in the cathetomete cathetometer scale. The error of the first kind was considered to be within ±0.005cm. Over the short length of the cathetometer scale which was required to determine Δl_c, the error of the second kind was thought to be a maximum of ± 0.002cm. The total error in Δl_c was taken to be ± 0.005cm. at low values of Δl_c and ± 0.007cm. at high values. The corresponding percentage uncertainties are ± 5% and ± 0.07%.

The overall error in x_2 is largely due to errors in Δl_c at high values of x_2 and to errors in A_c at low values of x_2. It is estimated that the uncertainty in x_2 around $x_2 = 0.9$ is about ± 0.0005 or ± 0.05% and around $x_2 = 0.1$, the uncertainty is ± 0.0001 or 0.1%.

2. **Errors in v^e.**

(a). Δl_E. The measured values of Δl_E were subject to the same sources of error as Δl_c. At low values of Δl_E, the uncertainty due to these was taken as ± 0.005cm., and at high values, the uncertainty was taken to be ± 0.007cm. A much greater source of inaccuracy was the thermal expansion of the liquids caused by changes in temperature of the thermostat. It was considered that, over the period of one experiment, the bath temperature was constant to within ± 0.002°C which resulted in an uncertainty in Δl_g of ± 0.07cm. The overall uncertainty in Δl_g was taken as ± 0.08cm. which varied as a percentage from 8% to 1%.

(b). A_g. The cross-sectional area was found to be 0.00126 ± 0.00004cm.^{2} or ±5%.

(c). n_1 and n_2. The limits of accuracy for n_1 and n_2 were much closer than those for Δl_g and A_g and could be ignored.

The overall uncertainty in v^{ϕ} was estimated to be about ± 12% at high values of x_2 and about ± 5% at low values. In terms of cm.^{3}mole^{-1}, this is about ± 0.0006 and ± 0.0003 cm.^{3} mole.$^{-1}$

Table 7.4.1.

Cyclohexane + t-butylcyclohexane. 20.00°C.

Mass t-BuCH = 2.7307_7g. ΔV^* Correction Term = 0.

Moles t-BuCH = $19.46_9 \times 10^{-3}$.

l_c cm.	x_2	l_g cm.	$\Delta V^*_{corr.}$ $cm^3. mole^{-1}$.	v^e $cm^3. mole^{-1}$.	Δv %.
0.105	0.9190	0.199	0.0132	0.0121	0.0072
0.221	0.8435	0.489	0.0316	0.0267	0.0164
0.507	0.7013	1.261	0.0814	0.0571	0.0371
0.808	0.5957	1.852	0.1196	0.0713	0.0458
1.197	0.4987	2.341	0.1512	0.0754	0.0537
1.819	0.3956	2.986	0.1928	0.0764	0.0571
2.989	0.2849	3.735	0.2111	0.0687	0.0463
4.682	0.2028	4.292	0.2771	0.0562	0.0452
10.179	0.1047	5.163	0.3333	0.0349	0.0304

Table 7.4.2.

Cyclohexane + t-butylcyclohexane. 40.03°C.

Mass t-BuCH = 3.0594_1g.

Moles t-BuCH = $21.81_2 \times 10^{-3}$. ΔV^* Correction Term = 0

l_c cm.	x_2	l_g cm.	$\Delta V^*_{corr.}$ $cm^3. mole^{-1}$.	v^e $cm^3. mole^{-1}$.	Δv %.
0.147	0.8192	0.324	0.0187	0.0167	0.0099
0.598	0.6887	1.302	0.0751	0.0517	0.0331
0.891	0.6001	1.749	0.1008	0.0605	0.0401
1.364	0.4969	2.259	0.1302	0.0647	0.0453
1.964	0.4080	2.696	0.1554	0.0634	0.0451
3.189	0.2988	3.226	0.1854	0.0556	0.0424
5.437	0.2003	3.734	0.2152	0.0431	0.0348

Table 7.4.3.

Cyclohexane + dicyclohexyl. 20.05°C.

Mass DCH = 2.9494_0g. $-\Delta V^*$ Correction Term = 0.

Moles DCH = $17.73_6 \times 10^{-3}$.

l_c cm.	x_2	$-l_E$ cm.	$-\Delta V^*_{corr.}$ cm^3. mole^{-1}.	$-v^e$ cm^3. mole^{-1}.	$-\Delta v$ %
0.117	0.9026	-0.013	-0.0009	-0.0008	-0.0004
0.259	0.8073	0.008	0.0006	0.0005	0.0003
0.476	0.6956	0.058	0.0041	0.0029	0.0018
0.681	0.614	0.095	0.0067	0.0041	0.0026
0.886	0.5504	0.183	0.0130	0.0072	0.0048
1.265	0.4616	0.594	0.0421	0.0194	0.0133
1.952	0.3572	0.855	0.0607	0.0217	0.0158
2.955	0.2685	1.074	0.0761	0.0204	0.0157
4.752	0.1859	1.380	0.0998	0.0182	0.0140

Table 7.4.4.

Cyclohexane + dicyclohexyl. 30.00°C.

Mass DCH = 2.6379_3g. $-\Delta V^*$ Correction Term = 0.

Moles DCH = $15.86_3 \times 10^{-3}$.

l_c cm.	x_2	$-l_E$ cm.	$-\Delta V^*_{corr.}$ cm^3. mole^{-1}.	$-v^e$ cm^3. mole^{-1}.	$-\Delta v$ %
0.109	0.9000	0.156	0.0124	0.0112	0.0066
0.220	0.8170	0.499	0.0275	0.0225	0.0129
0.524	0.6520	0.964	0.0635	0.0425	0.0264
0.698	0.5844	1.029	0.0815	0.0476	0.0305
0.922	0.5157	1.321	0.1047	0.0540	0.0360

Table 7.4.4. (contd.).

1.187	0.4526	1.576	0.1249	0.0565	0.0390
1.428	0.4074	1.804	0.1497	0.0610	0.0430
1.702	0.3658	2.037	0.1614	0.0590	0.0424
2.076	0.3216	2.337	0.1852	0.0596	0.0444
2.254	0.2800	2.606	0.2065	0.0578	0.0439

Cyclohexane + dicyclohexyl. 29.54°C.

Mass DCH = 2.6379_3g. $-\Delta V^*$ Correction Term = 0.

Moles DCH = $15.86_3 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_E$ cm.	$-\Delta V^*_{corr.}$ $cm^3.\ mole^{-1}$.	$-v^e$ $cm^3.\ mole^{-1}$.	$-\Delta v$ %
3.375	0.1952	1.587	0.250	0.0458	0.0396
4.730	0.1457	1.852	0.276	0.0402	0.0392
6.009	0.1187	2.048	0.295	0.0359	0.0295

Table 7.4.5.

Cyclohexane + dicyclohexyl. 40.00°C.

Mass DCH = 2.0481_1g. $-\Delta V^*$ Correction Term = 0.066cm³. mole⁻¹.

Moles DCH = $12.31_6 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_E$ cm.	$-\Delta V^*_{corr.}$ $cm^3.\ mole^{-1}$.	$-v^e$ $cm^3.\ mole^{-1}$.	$-\Delta v$ %
0.109	0.8763	0.835	0.041	0.0361	0.0161
0.165	0.8239	0.883	0.046	0.0380	0.0213
0.270	0.7409	1.106	0.069	0.0511	0.0304
0.438	0.6380	1.565	0.116	0.0740	0.0467
0.549	0.5844	1.798	0.139	0.0812	0.0518
0.799	0.4914	2.405	0.201	0.0987	0.0663

Table 7.4.5. (contd.)

1.008	0.4337	2.702	0.232	0.1005	0.0687
1.563	0.3306	3.400	0.303	0.1002	0.0728
2.997	0.2068	4.412	0.361	0.0739	0.0583
4.706	0.1409	5.032	0.469	0.0661	0.0564
6.040	0.1133	5.556	0.573	0.0593	0.0491

Table 7.4.6.

Cyclohexane + dicyclohexylmethane. 20.50°C.

Mass DCHM = 3.3109_6 g. $-\Delta V^*$ Correction Term = 0.

Moles DCHM = $19.91_0 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_t$ cm.	$-\Delta V^*_{corr.}$ $cm^3 . mole^{-1}$.	$-v^e$ $cm^3 . mole^{-1}$.	$-\Delta v$ %
0.074	0.9427	0.156	0.0098	0.0093	0.0047
0.133	0.9017	0.436	0.0275	0.0248	0.0127
0.224	0.8444	0.748	0.0472	0.0399	0.0209
0.342	0.7808	1.058	0.0668	0.0522	0.0284
0.434	0.7371	1.268	0.0881	0.0595	0.0321
0.531	0.6964	1.658	0.1056	0.0735	0.0418
0.656	0.6500	1.864	0.1200	0.0780	0.0453
0.824	0.5965	2.170	0.1370	0.0817	0.0492
1.010	0.5467	2.764	0.1745	0.0959	0.0596
1.240	0.4955	3.194	0.2017	0.1000	0.0641
1.532	0.4428	3.633	0.2294	0.1016	0.0673
1.854	0.3965	4.287	0.2707	0.1073	0.0730
2.272	0.3490	4.691	0.2965	0.1035	0.0728

Table 7.4.6. (contd.)

2.908	0.2952	5.295	0.3343	0.0987	0.0720
3.832	0.2412	6.038	0.3818	0.0919	0.0698
4.930	0.1980	6.458	0.4077	0.0808	0.0636
7.014	0.1477	7.145	0.4511	0.0667	0.0547
10.854	0.100	7.980	0.5038	0.0505	0.0431

Table 7.4.7.

Cyclohexane + dicyclohexylmethane. 39.99°C.

Mass DCHM = 2.6613_9g. $-\Delta V^*$ Correction Term = −0.014.

Moles DCHM = $14.75_9 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_g$ cm.	$-\Delta V^*_{corr.}$ cm^3. mole^{-1}.	$-V^E$ cm^3. mole^{-1}.	$-\Delta V$ %
0.095	0.9069	0.296	0.011	0.0101	0.0050
0.209	0.8157	0.919	0.064	0.0524	0.0274
0.384	0.7066	1.895	0.147	0.1041	0.0578
0.634	0.5934	3.069	0.247	0.1468	0.0875
0.912	0.5035	4.063	0.333	0.1672	0.1043
1.397	0.3984	5.530	0.457	0.1820	0.1213
2.178	0.2981	6.970	0.580	0.1728	0.1234
3.705	0.1998	8.980	0.751	0.1500	0.1127
8.726	0.0958	11.362	0.954	0.0914	0.0760

Table 7.4.8.

Cyclohexane + 1,2-dicyclohexylethane. 20.08°C.

Mass DCHE = 3.2676_3 g. $-\Delta V^*$ Correction Term = 0.

Moles DCHE = $16.81_4 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_s$ cm.	$-\Delta V^*_{corr.}$ $cm^3. mole^{-1}.$	$-v^e$ $cm^3. mole^{-1}.$	$-\Delta v$ %
0.020	0.9807	0.035	0.0026	0.0027	0.0014
0.111	0.9028	0.051	0.0038	0.0034	0.0016
0.199	0.8380	0.167	0.0125	0.0105	0.0052
0.243	0.8090	0.249	0.0186	0.0151	0.0076
0.358	0.7418	0.454	0.0340	0.0252	0.0131
0.431	0.7045	0.567	0.0424	0.0299	0.0160
0.544	0.6599	0.619	0.0463	0.0303	0.0166
0.703	0.5940	1.003	0.0750	0.0446	0.0255
0.846	0.5486	1.354	0.1013	0.0555	0.0326
1.024	0.5010	1.547	0.1157	0.0580	0.0352
1.279	0.4451	2.078	0.1554	0.0692	0.0434
1.538	0.4008	2.508	0.1876	0.0752	0.0485
1.923	0.3484	2.900	0.2168	0.0755	0.0510
2.471	0.2938	3.510	0.2625	0.0771	0.0546
3.160	0.2455	4.143	0.3098	0.0761	0.0560
4.241	0.1951	4.906	0.3669	0.0716	0.0551
5.906	0.1483	5.740	0.4292	0.0635	0.0509
9.291	0.0996	6.751	0.5048	0.0503	0.0423
12.363	0.0768	6.892	0.5154	0.0400	0.0342

Table 7.4.9.

Cyclohexane + 1,2-dicyclohexylethane. 40.21°C.

Mass DCHE = 2.9980_5 g. $-\Delta V^*$ Correction Term = $-0.025 cm^3.mole^{-1}$.

Moles DCHE = $15.42_6 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_g$ cm.	$-\Delta V^*_{corr.}$ $cm^3. mole^{-1}$.	$-v^E$ $cm^3. mole^{-1}$.	$-\Delta v$ %
0.070	0.9325	0.682	0.031	0.029	0.013
0.124	0.8863	1.057	0.061	0.054	0.025
0.225	0.8112	1.570	0.103	0.084	0.041
0.370	0.7513	2.101	0.146	0.110	0.056
0.472	0.6721	2.557	0.183	0.130	0.070
0.697	0.5811	3.346	0.248	0.144	0.081
0.989	0.4948	4.432	0.336	0.166	0.099
1.437	0.4022	5.568	0.429	0.173	0.109
2.233	0.3022	7.099	0.559	0.168	0.116
3.681	0.2081	8.912	0.701	0.146	0.108
8.339	0.1039	11.657	0.925	0.096	0.078

Table 7.4.10.

Cyclohexane + 1,3-dicyclohexylpropane. 20.00°C.

Mass DCHP = 3.3908_7 g. $-\Delta V^*$ Correction Term = 0.

Moles DCHP = $16.27_3 \times 10^{-3}$.

Δl_c cm.	x_2	$-\Delta l_g$ cm.	$-\Delta V^*_{corr.}$ $cm^3. mole^{-1}$.	$-v^E$ $cm^3. mole^{-1}$.	$-\Delta v$ %
0.118	0.8940	0.128	0.0099	0.0089	0.0040
0.250	0.7992	0.483	0.0373	0.0298	0.0140
0.519	0.6573	0.984	0.0760	0.0500	0.0256
0.663	0.6002	1.275	0.0985	0.0591	0.0317

Table 7.4.10. (contd.).

0.912	0.5218	1.858	0.1420	0.0741	0.0421
1.168	0.4599	2.425	0.1873	0.0861	0.0513
1.715	0.3672	3.450	0.2673	0.0979	0.0628
2.313	0.3008	4.097	0.3165	0.0952	0.0646
3.890	0.2137	6.005	0.4638	0.0965	0.0689

Table 7.4.11.

Cyclohexane + 1,3-dicyclohexylpropane. 39.99°C.

Mass DCHP = 3.3908$_7$g. $-\Delta V^*$ Correction Term = -0.0218cm^3.mole^{-1}.

Moles DCHP = 16.84$_1$ X 10^{-3}.

Δl_c cm.	x_2	$-\Delta l_E$ cm.	$-\Delta V^*_{corr.}$ cm^3. mole^{-1}.	$-V^E$, cm^3. mole^{-1}.	$-\Delta V$ %
0.171	0.8605	0.767	0.0354	0.0305	0.0136
0.278	0.7913	0.995	0.0525	0.0415	0.0193
0.430	0.7105	1.385	0.0816	0.0580	0.0284
0.816	0.5640	2.802	0.1873	0.1056	0.0571
0.959	0.5238	3.403	0.2322	0.1216	0.0676
1.064	0.4979	3.940	0.2723	0.1356	0.0768
1.291	0.4498	4.716	0.3302	0.1485	0.0872
1.560	0.4034	5.557	0.3930	0.1585	0.0966
1.953	0.3508	6.959	0.4976	0.1746	0.1112
2.393	0.3060	8.122	0.5844	0.1788	0.1182
3.166	0.2500	9.370	0.6776	0.1694	0.1174
4.241	0.1992	9.891	0.7159	0.1476	0.1051
5.934	0.1510	10.393	0.7537	0.1138	0.0870
9.700	0.1031	13.223	0.9649	0.0995	0.0800
12.229	0.0794	13.864	1.013	0.0804	0.0663

Table 7.4.12.

Cyclohexane + t-butylcyclohexane.

x_2	$-\left(\frac{dv^{e}}{dT}\right)^{20-40^\circ C}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00060
0.2	0.00071
0.3	0.00061
0.4	0.00063
0.5	0.00058
0.6	0.00053
0.7	0.00037
0.8	0.00022
0.9	0.00004

Table 7.4.13.

Cyclohexane + dicyclohexylmethane.

x_2	$-\left(\frac{dv^{e}}{dT}\right)^{20-40^\circ C}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00204
0.2	0.00338
0.3	0.00375
0.4	0.00385
0.5	0.00457
0.6	0.00307
0.7	0.00180
0.8	0.00082
0.9	0.00030

Table 7.4.14.

Cyclohexane + dicyclohexyl.

x_2	$-\frac{1}{2}\left(\frac{dv^{e}}{dT}\right)^{20-30^\circ C}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00102
0.2	0.00115
0.3	0.00114
0.4	0.00177
0.5	0.00203
0.6	0.00197
0.7	0.00170
0.8	0.00126
0.9	0.00066

Table 7.4.15.

Cyclohexane + dicyclohexyl.

x_2	$-\frac{1}{2}\left(\frac{dv^{e}}{dT}\right)^{30-40^\circ C}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00086
0.2	0.00105
0.3	0.00184
0.4	0.00216
0.5	0.00212
0.6	0.00168
0.7	0.00124
0.8	0.00087
0.9	0.00047

Table 7.4.16.

Cyclohexane + 1,2-dicyclohexylethane.

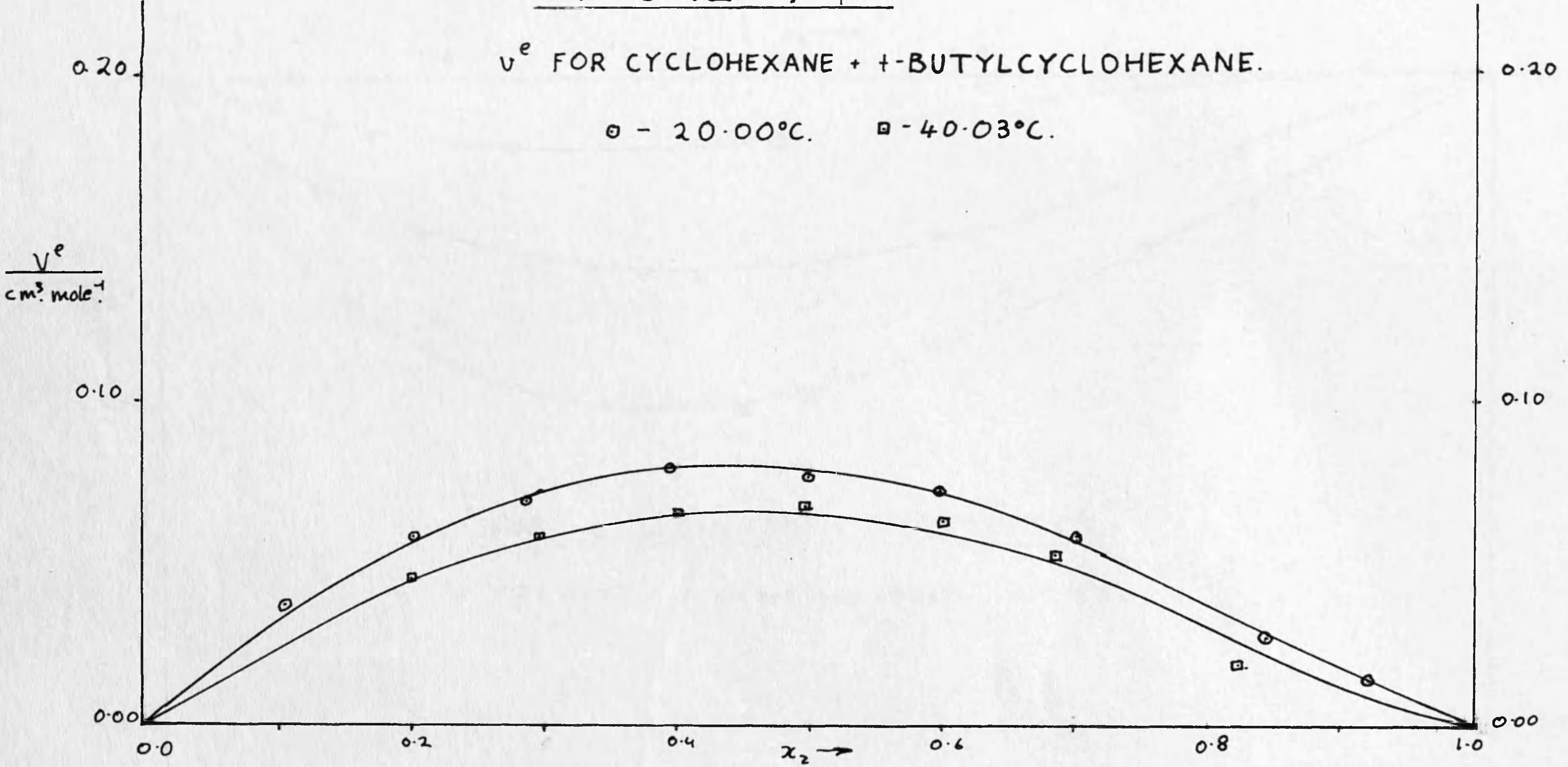
x_2	$-\left(\frac{dv^{e}}{dT}\right)^{20-40^{\circ}C}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00207
0.2	0.00351
0.3	0.00447
0.4	0.00499
0.5	0.00519
0.6	0.00488
0.7	0.00464
0.8	0.00364
0.9	0.00217

Table 7.4.17.

Cyclohexane + 1,3-dicyclohexylpropane.

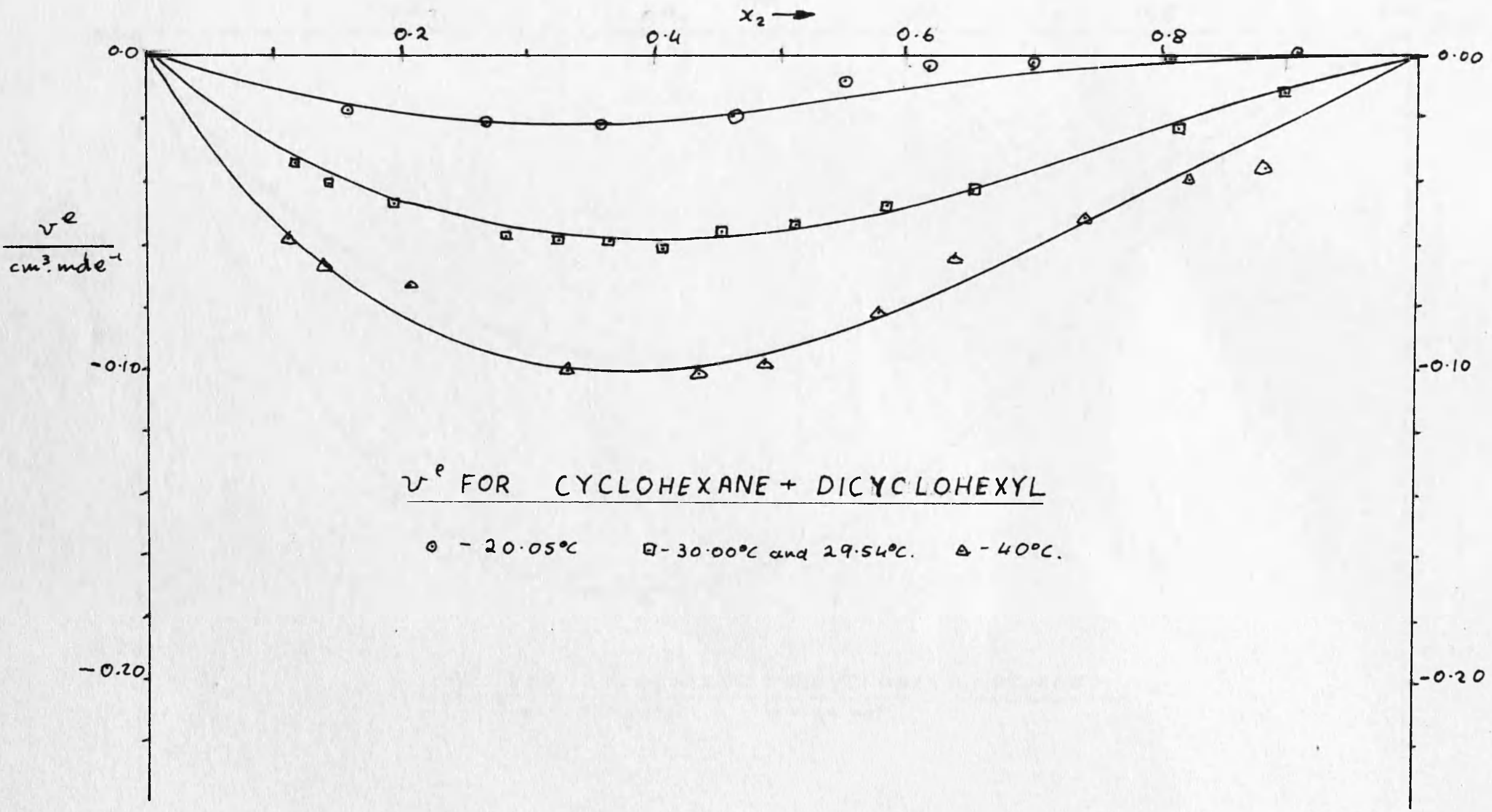
x_2	$-\left(\frac{dv^{e}}{dT}\right)^{20-40^{\circ}C.}$ cm^3.mole^{-1}.deg^{-1}.
0.1	0.00175
0.2	0.00320
0.3	0.00356
0.4	0.00348
0.5	0.00257
0.6	0.00153
0.7	0.00093
0.8	0.00062
0.9	0.00041

FIGURE 7.4.1.



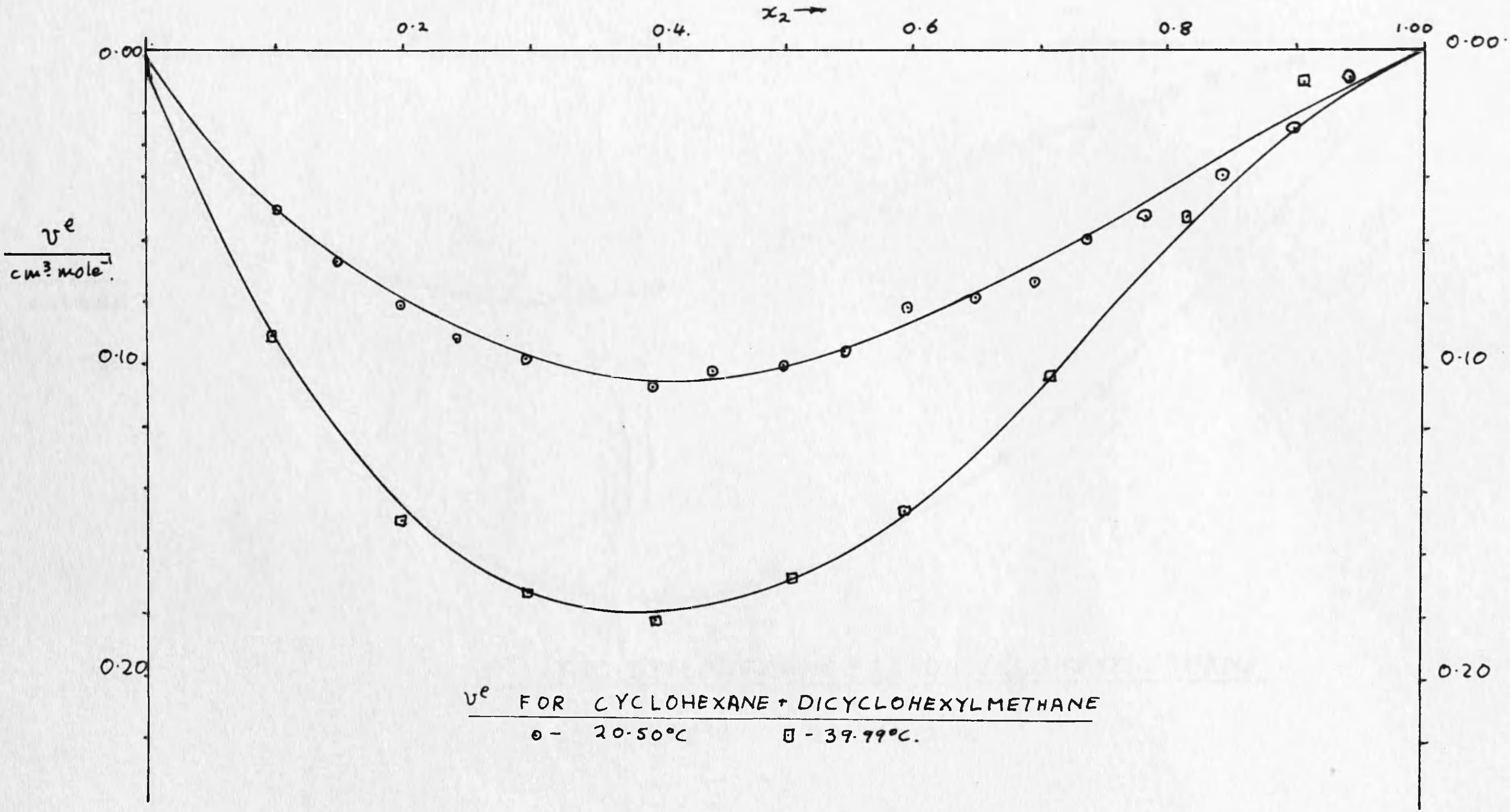
v^e FOR CYCLOHEXANE + t-BUTYLCYCLOHEXANE.

FIGURE 7.4.2.



v^e FOR CYCLOHEXANE + DICYCLOHEXYL

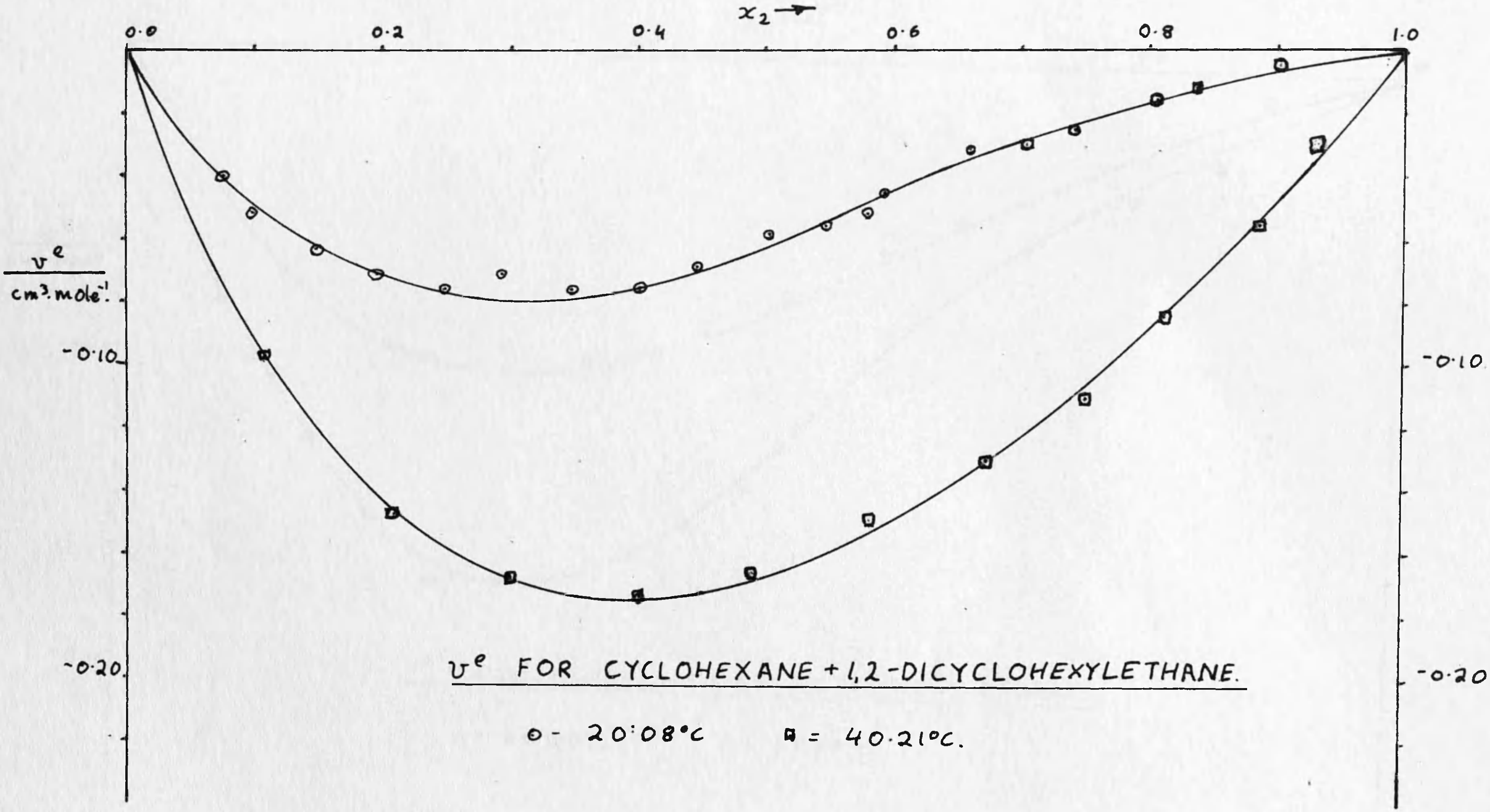
FIGURE 7.4.3.



v^e FOR CYCLOHEXANE + DICYCLOHEXYLMETHANE

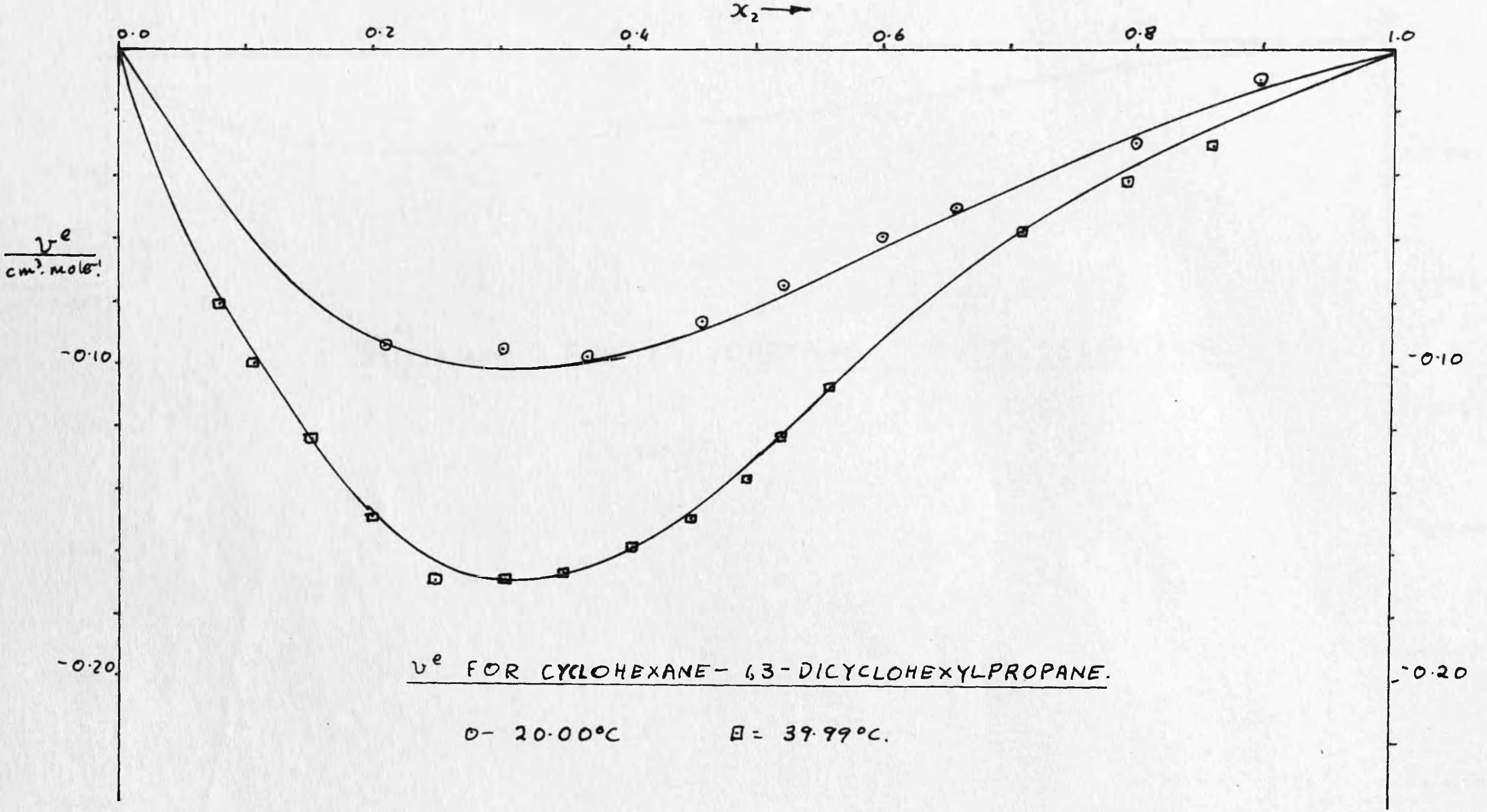
⊙ - 20·50°C ⊡ - 39·99°C.

FIGURE 7.4.4.



v^e FOR CYCLOHEXANE + 1,2-DICYCLOHEXYLETHANE.

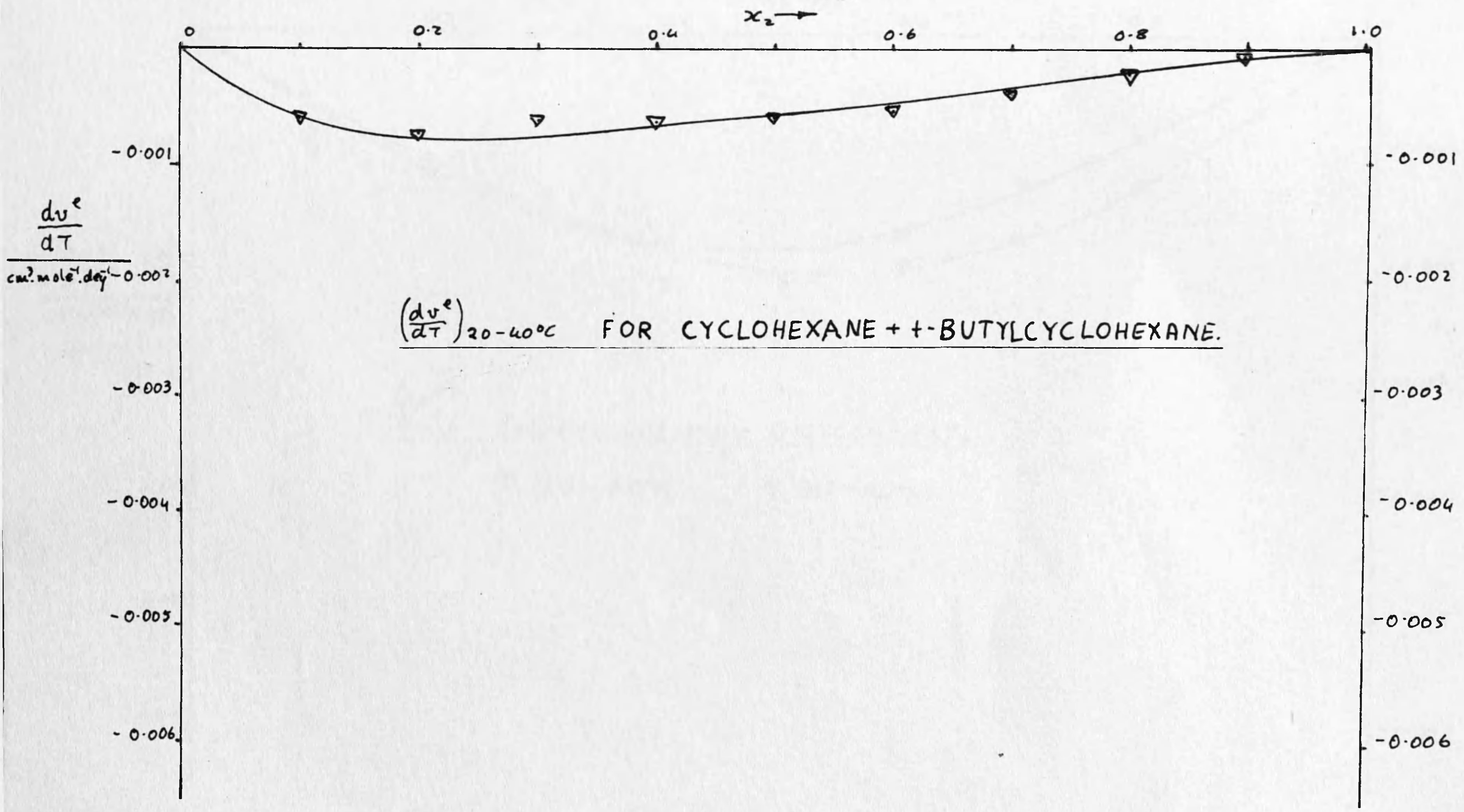
FIGURE 7.4.5.



v^e FOR CYCLOHEXANE – 1,3 - DICYCLOHEXYLPROPANE.

○ – 20.00°C ⊡ = 39.99°C.

FIGURE 7.4.6.



$\left(\frac{dv^e}{dT}\right)_{20-40°C}$ FOR CYCLOHEXANE + t-BUTYLCYCLOHEXANE.

FIGURE 7.4.7.

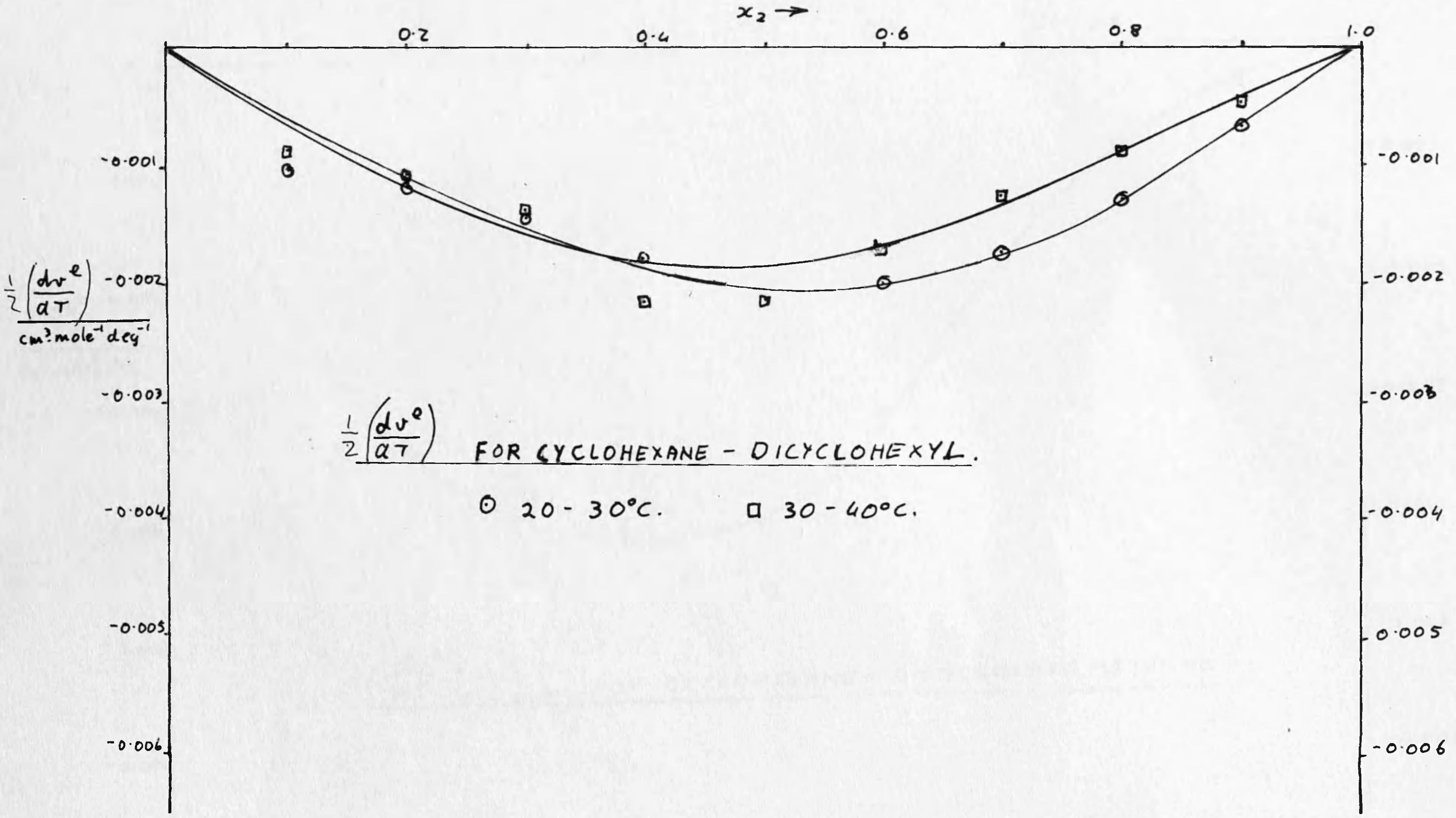
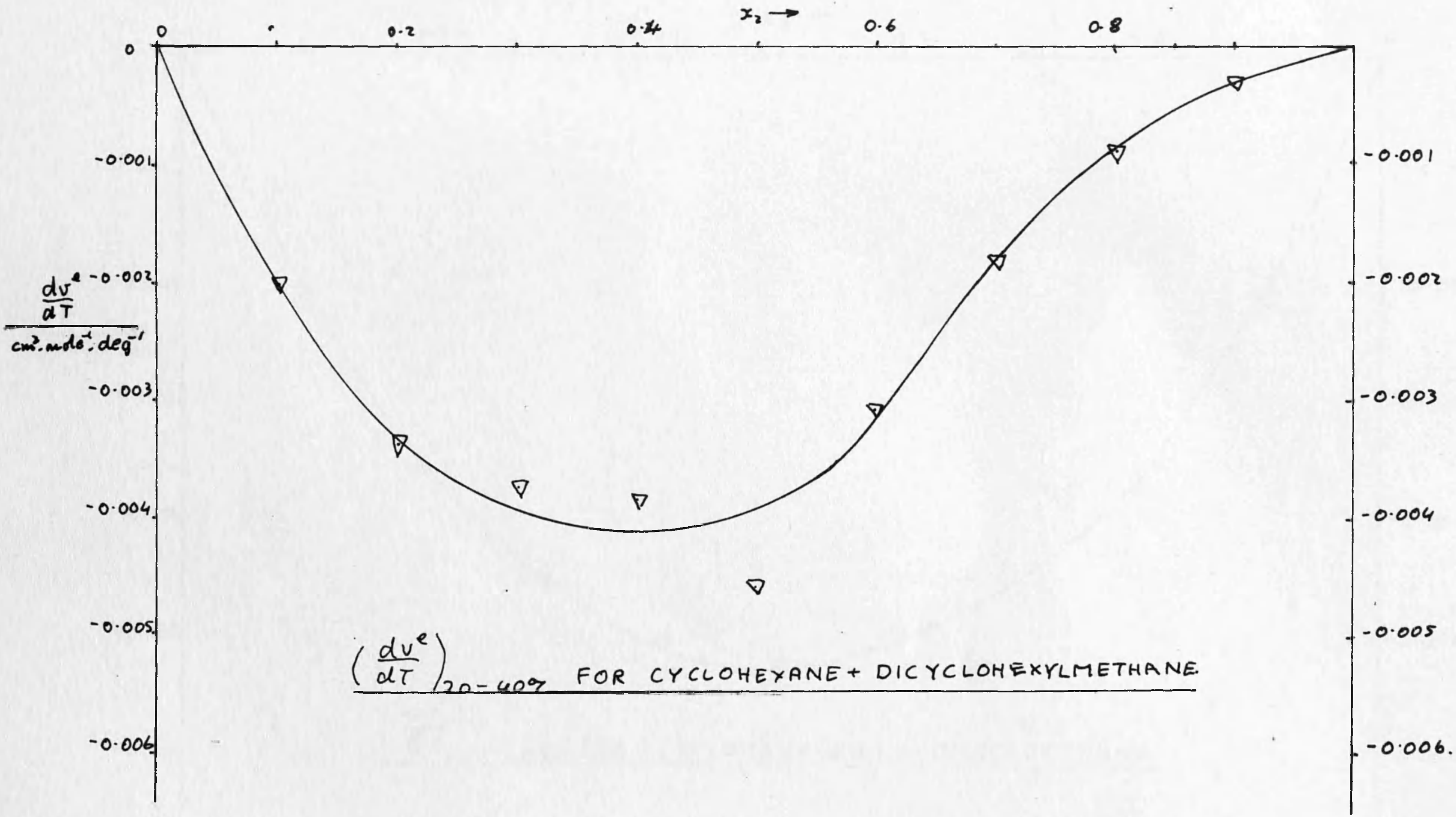
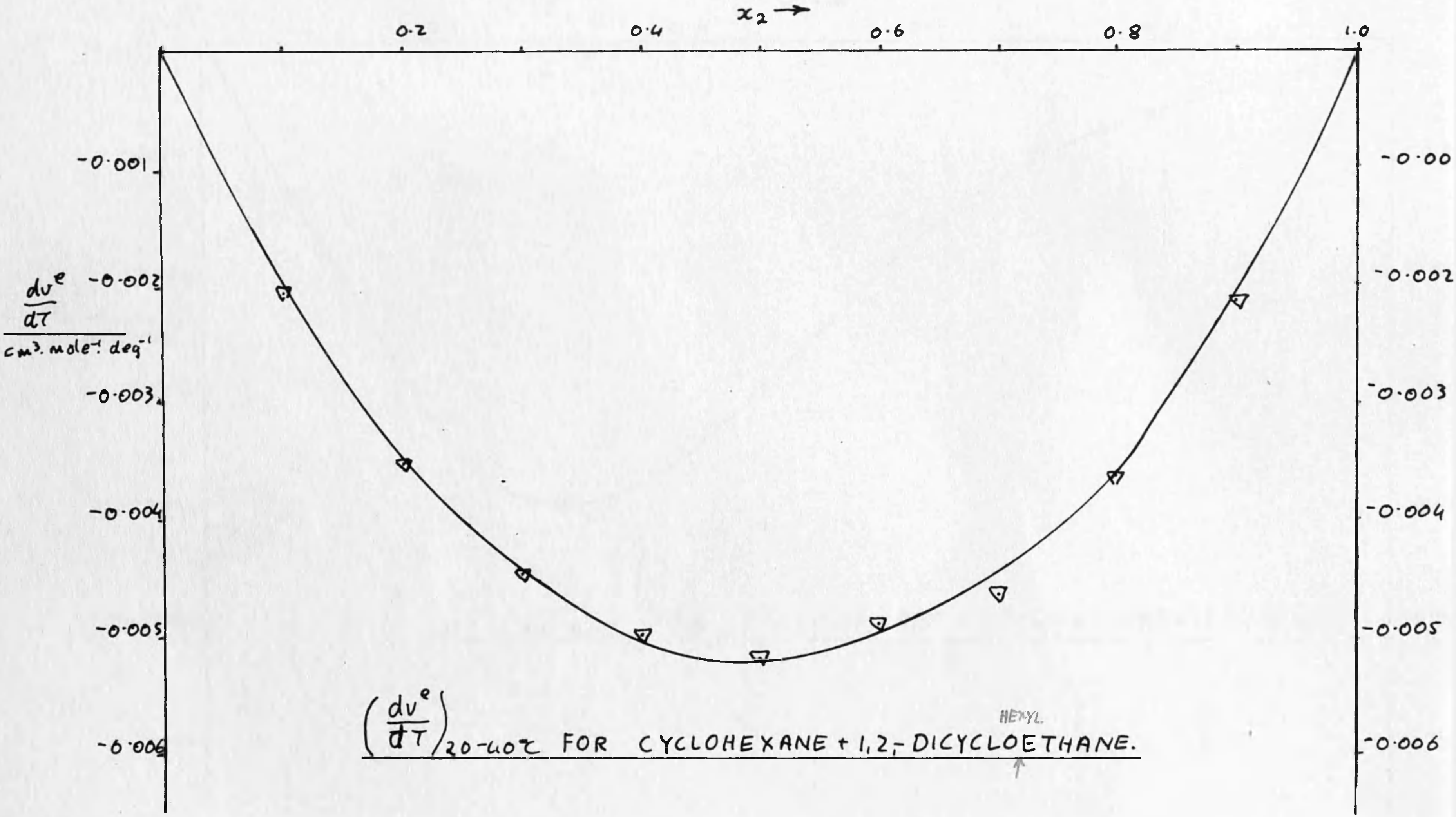

$\frac{1}{2}\left(\frac{dv^e}{dT}\right)$ FOR CYCLOHEXANE - DICYCLOHEXYL.

FIGURE 7.4.8.



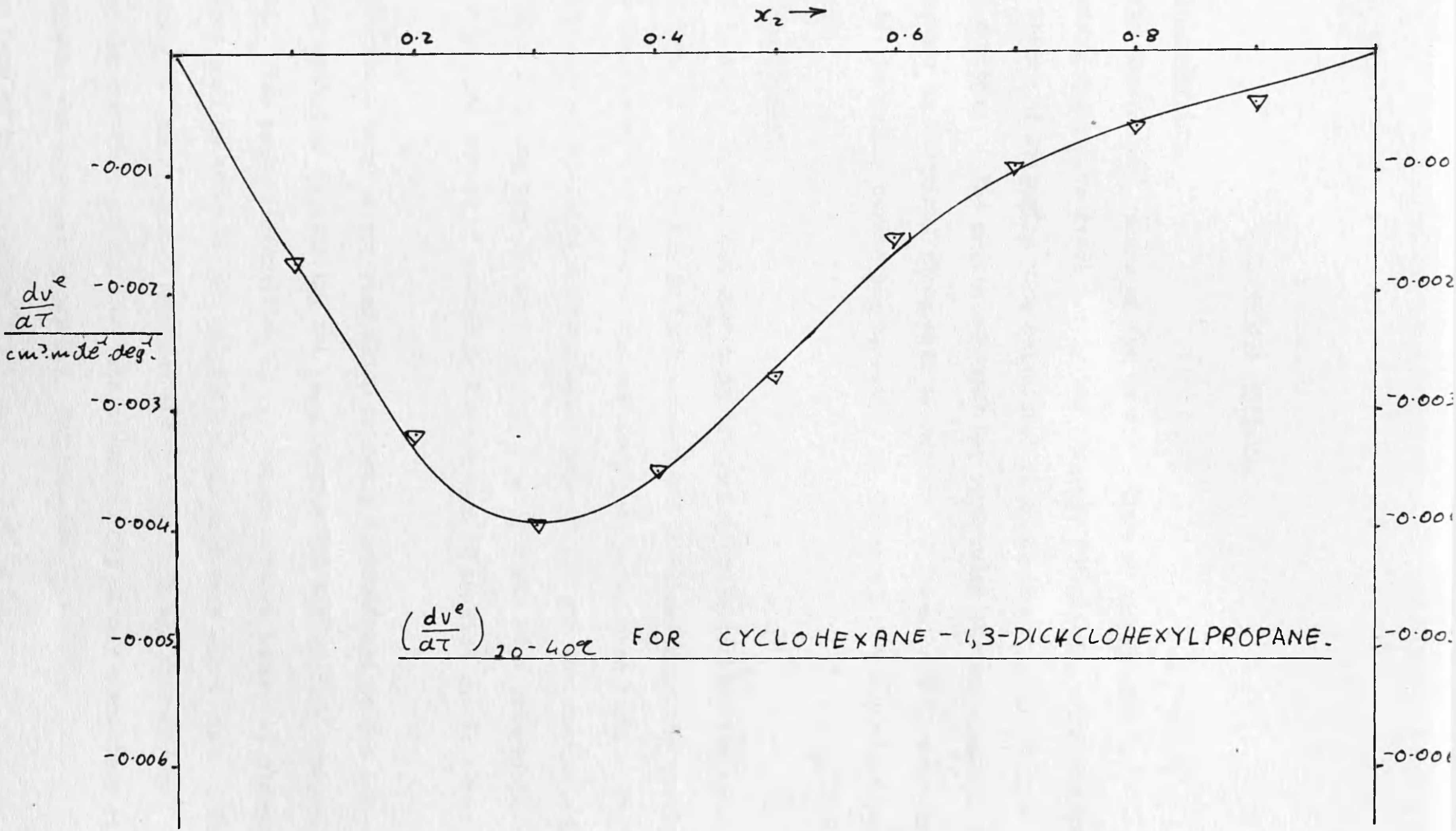
$\left(\frac{dv^e}{dT}\right)_{20-40°}$ FOR CYCLOHEXANE + DICYCLOHEXYLMETHANE

FIGURE 7.4.9.



$\left(\frac{dv^e}{dT}\right)_{20-40°C}$ FOR CYCLOHEXANE + 1,2,-DICYCLOHEXYLETHANE.

FIGURE 7.4.10.



$\left(\frac{dv^e}{dT}\right)_{20-40°C}$ FOR CYCLOHEXANE - 1,3-DICYCLOHEXYLPROPANE.

Chapter 8.

Theoretical Results.

8.1. Introduction.

The theoretical values of the excess volume of mixing and its temperature derivative predicted by the 'Average Potential', corresponding States theory of Prigogine were calculated from equation 3.5.13 using a digital computer. The method employed for performing the calculations with the computer is described along with an account of the methods whereby the values of the various parameters appearing in the explicit expressions were obtained.

8.2. The Computer.

A 'Sirius' digital computer manufactured by Ferranti Ltd. was used. Punched tape is used to supply instructions and information to the machine and the results of the calculations are received in the same form. The input tapes are prepared on a conventional teleprinter and the results are transcribed from the tape to typed format also by means of a teleprinter.

The general method of operating the machine is carried out in three steps.

1. A programme tape is prepared which contains instructions to the computer as to the method of calculating the results from the information subsequently supplied. The machine calculates by performing a large number of elementary operations such as addition and multiplication in a very short time. The preparation of the programme tape for the present work was preceded by breaking the equation 3.5.13 down into approximately ninety elementary steps. The programme was prepared by Dr. F.L. Swinton.

The form of the expression 3.5.13 can be seen to be,

$$v^E = A v_1 + BT \frac{dv_1}{dT} + CT^2 \frac{d^2 v_1}{dT^2} \qquad 8.2.1.$$

8.2.1.

where A, B, and C are terms which do not depend on the temperature. The value of $\frac{dv^e}{dT}$ is determined by differentiation giving,

$$\frac{dv^e}{dT} = A\frac{dv_1}{dT} + B\left(T\frac{d^2v_1}{dT^2} + \frac{dv_1}{dT}\right) + C\left(2T\frac{d^2v_1}{dT^2} + T^2\frac{d^3v_1}{dT^3}\right) \tag{8.2.2.}$$

It is clear that if A, B and C are calculated for v^e, the value of $\frac{dv^e}{dT}$ can be readily calculated using them, if the values of the properties of the pure reference substance in the brackets of equation 8.2.2. are known. The evaluation of the terms within the brackets is described in section 8.5.

2. The instructions supplied on the programme tape are stored in the machine and come into operation when the values of θ, ρ, and δ, which are the only parameters which vary from system to system, are supplied on a short data tape. The data tape contains values of θ, ρ, and δ which are selected for various situations of interest.

3. After the machine has performed the desired calculations, the results appear on a results tape. The information on this tape is transcribed by the teleprinter and is obtained in a typed format. The output of the machine for the present purpose, was arranged so that the selected values of θ, ρ and δ were printed first followed by the corresponding values of v^e and $\frac{dv^e}{dT}$ at rounded mole fractions, $x_2 = 0.1$, 0.2 etc. An example of the results from the computer is shown in Table 8.2.1.

Separate calculations were made for v^e at 20°C. and 40°C. using appropriate values of the properties v_1, $\frac{dv_1}{dT}$ etc. which appear in equations 8.2.1. and 8.2.2.

The machine performed the calculations for the excess volume of mixing - composition relationship over the full composition range in twenty-nine seconds. This task, when performed normally using a desk calculator required up to nine days.

Due to the speed of the computer, it was easier, quicker and more accurate to investigate the dependence of v^e on various terms in equation 3.5.13 by simply calculating v^e for different values of the quantity of interest, all other quantities being held constant, rather than by an analytical method using complicated algebra.

8.3. The Evaluation of the Invariant Parameters.

In the equation 3.5.13 various parameters appear which describe the structure and size of the r-mer molecules. The present work is confined to mixtures of monomer-dimer type and the following values were used in all calculations.

$$z = 6 \text{ or } 12$$

$$r_1 = 1 \quad r_2 = 2$$

$$q_1 = 1 \quad q_2 = \frac{10}{6} \text{ or } \frac{11}{6}$$

$$c_1 = 1 \quad c_2 = \frac{5}{3}$$

The two values of q_2 reflect the two values of z which were employed.

8.4. The Evaluation of the Interaction Parameters θ, ρ and δ.

The definitions of θ, ρ, and δ may be recalled as

$$\theta = \frac{1}{\varepsilon_{11}^*}\left[\varepsilon_{12}^* - \frac{\varepsilon_{11}^* + \varepsilon_{22}^*}{2}\right] \tag{8.4.1.}$$

$$\rho = \frac{r_{22}^* - r_{11}^*}{r_{11}^*} \tag{8.4.2.}$$

$$\delta = \frac{1}{\varepsilon_{11}^*}\left[\varepsilon_{22}^* - \varepsilon_{11}^*\right] \tag{8.4.3.}$$

Only ρ and δ were obtained directly from experimental measurements. For systems composed of mixtures of molecules of similar size, ρ and δ

can be obtained from values of the critical properties, latent heats of sublimation of the pure components of the mixture, or values of ε^*_{11}, r^*_{11} etc. obtained from second virial co-efficient or gas viscosity measurements.[56] Methods using these quantities are of little use for mixtures of r-mers and the method generally used, employs the molar volumes of the two components as a function of temperature.[57] A brief outline of the theory of the method is useful.

The equation of state of liquids which follow the same Principle of Corresponding States, at zero pressure, in terms of the reduced volume and temperature, $\tilde{V}$ and $\tilde{T}$, is given by

$$\tilde{V} = \phi(\tilde{T}) \qquad 8.4.4.$$

where ϕ is a universal function of the reduced temperature. For a monomer, such as cyclohexane in the present work, this may be written,

$$\tilde{V} = \frac{v_1}{N v^*_{11}} = \phi\left(\frac{kT}{\varepsilon^*_{11}}\right) = \phi(\tilde{T}) \qquad 8.4.5.$$

and for an r-mer, such as dicyclohexylmethane,

$$\frac{v_2}{N r v^*_{22}} = \phi\left(\frac{kT\left(1 + \frac{r}{3}\right)}{\varepsilon^*_{11}\, q(1+\delta)}\right) \qquad 8.4.6.$$

At the same reduced temperature,

$$\tilde{V}_1 = \tilde{V}_2 \qquad 8.4.7.$$

ie.

$$\frac{v_1}{N v^*_{11}} = \frac{v_2}{N r v^*_{22}} \qquad 8.4.8.$$

and

$$\tilde{T}_1 = \tilde{T}_2 \qquad 8.4.9.$$

ie.

$$\frac{kT_1}{\varepsilon^*_{11}} = \frac{kT_2\left(1 + \frac{r}{3}\right)}{\varepsilon^*_{11}\, q(1+\delta)} \qquad 8.4.10.$$

Clearly then if equation 8.4.5. is written as,

$$v_1 = f(T_1) \qquad 8.4.11.$$

where f is a universal function of the absolute temperature incorporating the reducing factors v_{11}^* etc. It follows then also from equation 8.4.8. or 8.4.9. that,

$$\frac{v_2}{r}\left(\frac{v_{11}^*}{v_{22}^*}\right) = f\left(\frac{T_2\left(1+\frac{r}{3}\right)}{q(1+\delta)}\right) \qquad 8.4.12.$$

where f is the same function.

This may be re-written as

$$\frac{v_2}{\mu} = f\left(\frac{T_2}{\lambda}\right) \qquad 8.4.13.$$

where

$$\mu = r\left(\frac{v_{22}^*}{v_{11}^*}\right) = r\left(\frac{r_{22}^*}{r_{11}^*}\right)^3 = r(1+\rho)^3 \qquad 8.4.14.$$

and

$$\lambda^{-1} = \frac{\left(1+\frac{r}{3}\right)}{q(1+\delta)} \qquad 8.4.15.$$

The form of 8.4.13. means that, if the values of the molar volumes of the dimer component v_2, divided by a suitable value of μ are plotted on a graph against the corresponding absolute temperatures reduced by an appropriate value of λ, the resulting curve should be superimposable on the curve obtained by plotting v_1 against T_1 for the monomer. If the two components obey the same theorem of corresponding states, and good values of the reducing factors μ and λ are chosen, the superimposition obtained is very good and the values of ρ and δ can be calculated from equations 8.4.14 and 8.4.15.

This method was employed in the present work. The molar volumes of cyclohexane, obtained from the A.P.I. Tables were plotted against the absolute temperature on a large scale graph which was transferred to tracing paper. The values of the molar volumes of each of the dimer components at a wide range of temperature were obtained by direct measurements. The values of v_2 and T_2 were reduced by different values of μ and λ until a pair of values were found which gave a curve of $\frac{v_2}{\mu}$ v $\frac{T_2}{\lambda}$ which exactly matched the v_1 v T_1 curve for cyclohexane. The values of ρ and δ were then calculated. These values are shown in Table 8.4.1. Since the expression for δ contains q, which is dependent on the number of nearest neighbours in the cell, z, the values of δ have been given for the values $z = 6$ and $z = 12$ which were of interest.

The limits of accuracy are those estimated from the calculations and give the limits within which no improvement in the fit of the two curves could be obtained. It is noticeable that the accuracy of ρ is superior to that of δ. This is due to the extraction of the cube root in equation 8.4.13. which reduces the uncertainty by a factor of three.

The molar volumes of the dimer components were obtained by measuring their densities from room temperature to just over 200°C. Modified Sprengel type pyknometers[85] were used and were calibrated using distilled, deionized water at 20°C. or 25°C. The densities of water $d^{t}_{4\,H_2O}$ were taken from Weissberger.[114] The changes in capacity of the pyknometers were calculated assuming a constant value for the co-efficient of thermal expansion of borosilicate glass of 3.09×10^{-5} deg.$^{-1}$ over the range of temperatures 20°C to 200°C.[115] Weighings were made to ± 0.00004 g. and the normal buoyancy corrections were applied. No corrections were made for vapour in the pyknometers above the mark but the pyknometer caps were flushed with air just before adjusting the liquid level to the mark.

The densities were determined at temperatures up to 60°C using a water thermostat controlled to ± 0.01 deg. C and at higher temperatures using a bath of silicone oil whose temperature was controlled to ± 0.5 deg.C. Temperatures below 100°C were measured using N.P.L. calibrated thermometers and were accurate to within ± 0.01 deg. C. Emergent stem corrections were applied. Temperatures above 100°C were measured using a Stantel F23 type thermistor which was calibrated up to 100°C by comparison with N.P.L. thermometer, and between 100°C and 150°C by comparison with a reliable although less accurate thermometer. Temperatures in excess of 150°C were calculated using the extrapolated calibration. The thermistor measured temperatures were taken to be reliable to ± 0.1°C.

The values of the densities and molar volumes of all the components are given in Tables 8.4.2. to 8.4.7. The plots of $\frac{v_2}{\mu}$ and $\frac{T_2}{\lambda}$ for all five systems are given in Figures 8.4.1. to 8.4.5.

No simple method is available for estimating θ. For spherical molecules of similar size, which interact through dispersion forces only, the geometric mean rule,

$$\varepsilon_{12} = \left(\varepsilon^{*}_{11}\,\varepsilon^{*}_{22}\right)^{\frac{1}{2}} \qquad 8.4.15.$$

should apply. This results in the following expression for θ.

$$\theta = -\frac{\delta^2}{8} \qquad 8.4.16.$$

There is little reason for using the geometric mean rule since the components are neither truly spherical nor of similar size. The values of θ calculated for 8.4.16 were obtained and are given in Table 8.4.1.

8.5. The Evaluation of the Properties of the Reference Substance.

Cyclohexane was chosen as the reference substance, therefore the

Table 8.4.2

The Densities and Molar Volumes of Cyclohexane.

Temperature. t^oC	Temperature. T^oK	d_4^t $g.cm^{-3}$	Molar Volume. Mol. Wt.=84.156 $cm^3.mole^{-1}$.
20.00	293.15	0.7786	108.09
30.00	303.15	0.7693	109.39
40.00	313.15	0.7598	110.76
50.00	323.15	0.7501	112.19
60.00	333.15	0.7405	113.65
70.00	343.15	0.7309	115.14
80.00	353.15	0.7212	116.69

Table 8.4.3

The Densities and Molar Volumes of Dicyclohexyl.

Temperature. t^oC	Temperature. T^oK	d_4^t $g.cm.^{-3}$	Molar Volume. Mol. Wt.=166.29_6 $cm^3.mole^{-1}$.
25.00	298.15	0.8823_8	188.46
30.00	303.15	0.8788_6	189.22
40.02	313.17	0.8717_3	190.77
50.03	323.18	0.8645_9	192.34
60.03	333.18	0.8574_7	193.94
80.22	353.37	0.8432_0	197.22
100.08	373.23	0.8287_9	200.65

Table 8.4.3. (contd.)

120.0	393.2	0.8147_9	204.10
140.0	413.2	0.8015_2	207.48
159.9	433.0	0.7860_8	211.55
180.1	453.2	0.7708_4	215.73
200.0	473.1	0.7549_6	220.27
211.5	484.7	0.7462	222.86

Table 8.4.4.

The Densities and Molar Volumes of Dicyclohexylmethane.

Temperature. t°C	Temperature. T°K	d_4^t g.cm.$^{-3}$	Molar Volume. Mol. Wt.=180.32_2 cm^3.mole^{-1}.
25.00	298.15	0.8731_6	206.52
30.00	303.15	0.8696_3	207.36
40.02	313.17	0.8624_2	209.09
50.03	323.18	0.8552_9	210.83
60.03	333.18	0.8483_5	212.56
80.22	353.37	0.8341_2	216.18
100.08	373.23	0.8202_7	219.83
120.0	393.15	0.8062_2	223.66
140.0	413.15	0.7918_1	227.73
160.0	433.12	0.7775_0	231.93
180.0	453.15	0.7625_2	236.48
200.0	473.10	0.7465_1	241.55

Table 8.4.5.

The Densities and Molar Volumes of 1,2-Dicyclohexylethane.

Temperature. t^oC	Temperature. T^oK	d_4^t $g.cm.^{-3}$	Molar Volume. Mol. Wt.=194.348 $cm^3.mole^{-1}$.
25.00	298.15	0.8738_7	222.40
30.00	303.15	0.8705_4	223.25
40.02	313.17	0.8634_9	225.07
50.03	323.18	0.8565_4	226.90
60.03	333.18	0.8498_1	228.70
80.22	353.37	0.8350_5	232.74
100.08	373.23	0.8231_6	236.01
120.00	393.15	0.8084_6	240.39
140.00	413.15	0.7945_0	244.62
160.00	433.15	0.7815_2	248.68
179.8	452.92	0.7669_1	253.42
199.9	473.02	0.7513_7	258.66

Table 8.4.6.

The Densities and Molar Volumes of 1,3-Dicyclohexylpropane.

Temperature. t^oC	Temperature. T^oK	d_4^t $g.cm.^{-3}$	Molar Volume. Mol. Wt.=208.374. $cm^3.mole^{-1}$.
24.80	297.95	0.8688_6	239.83
100.1	373.78	0.8181_8	254.68
119.9	393.08	0.8050_5	258.83
144.1	417.20	0.7879_8	264.44

Table 8.4.6. (contd.)

160.3	433.44	0.7765_6	268.32
178.9	452.04	0.7633_4	272.97
198.5	471.61	0.7496_3	277.96
215.6	488.74	0.7432_8	280.33

Table 8.4.7.

The Densities and Molar Volumes of t-Butylcyclohexane.

Temperature. $t^{o}C$	Temperature. $T^{o}K$	d_4^t $g.cm.^{-3}$	Molar Volume. Mol. Wt.=140.260 $cm^3.mole^{-1}$.
30.10	303.25	0.8023_7	174.81
39.97	313.12	0.7945_9	176.52
49.80	322.95	0.7881_2	177.97
69.92	343.07	0.7759_0	180.77
98.84	371.99	0.7516_6	186.60
129.9	403.09	0.7256_4	193.29
144.1	417.20	0.7135_0	196.58

Table 8.4.1.

The Values of δ and ρ obtained from Densities.

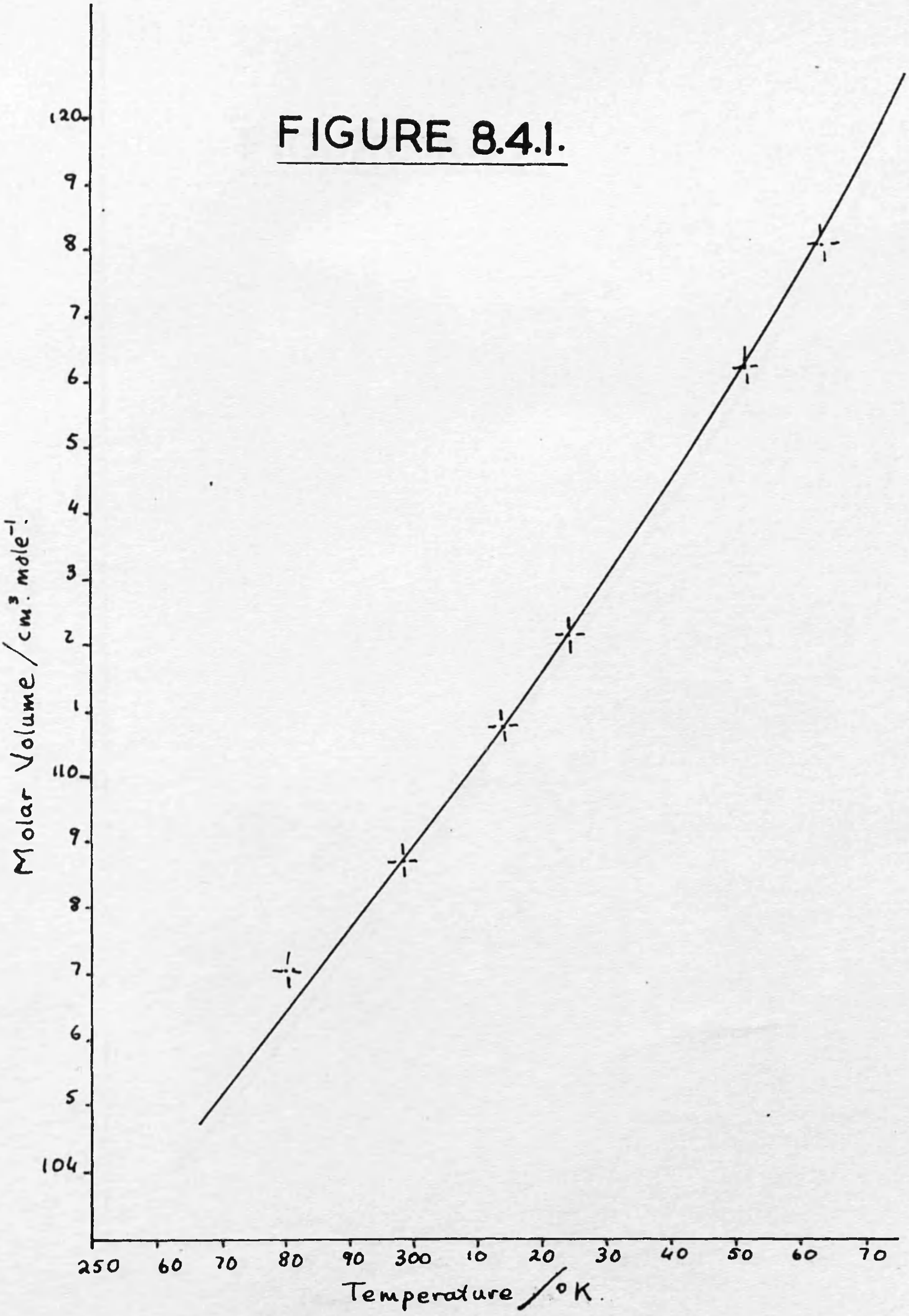
System	δ z=12	δ z=6	ρ.
Cyclohexane + t-Butylcyclohexane.	0.05	0.15	-0.06
Cyclohexane + Dicyclohexyl.	0.23	0.35	-0.018_5
Cyclohexane + Dicyclohexylmethane.	0.23	0.35	$+0.012_0$
Cyclohexane + 1,2-Dicyclohexylethane.	0.25	0.37	$+0.039_0$
Cyclohexane + 1,3-Dicyclohexylpropane.	0.26	0.38	$+0.065_5$
	± 0.02	± 0.02	± 0.002

Table 8.5.1.

The Properties of the Reference Substance, Cyclohexane.

	20°C.	40°C.	25°C. (Scott).
v_1	108.10_2	110.80_1	108.74
$T\frac{dv_1}{dT}$	38.22	43.84	38.99
$\frac{1}{2}T^2\frac{d^2v_1}{dT^2}$	17.40	27.56	22.23
$\frac{dv_1}{dT}$	0.1304	0.1401	0.133
$T\frac{d^2v_1}{dT^2}+\frac{dv_1}{dT}$	0.249	0.316	0.282
$T^2\frac{d^3v_1}{dT^3}+2T\frac{d^2v_1}{dT^2}$	0.912	1.123	–

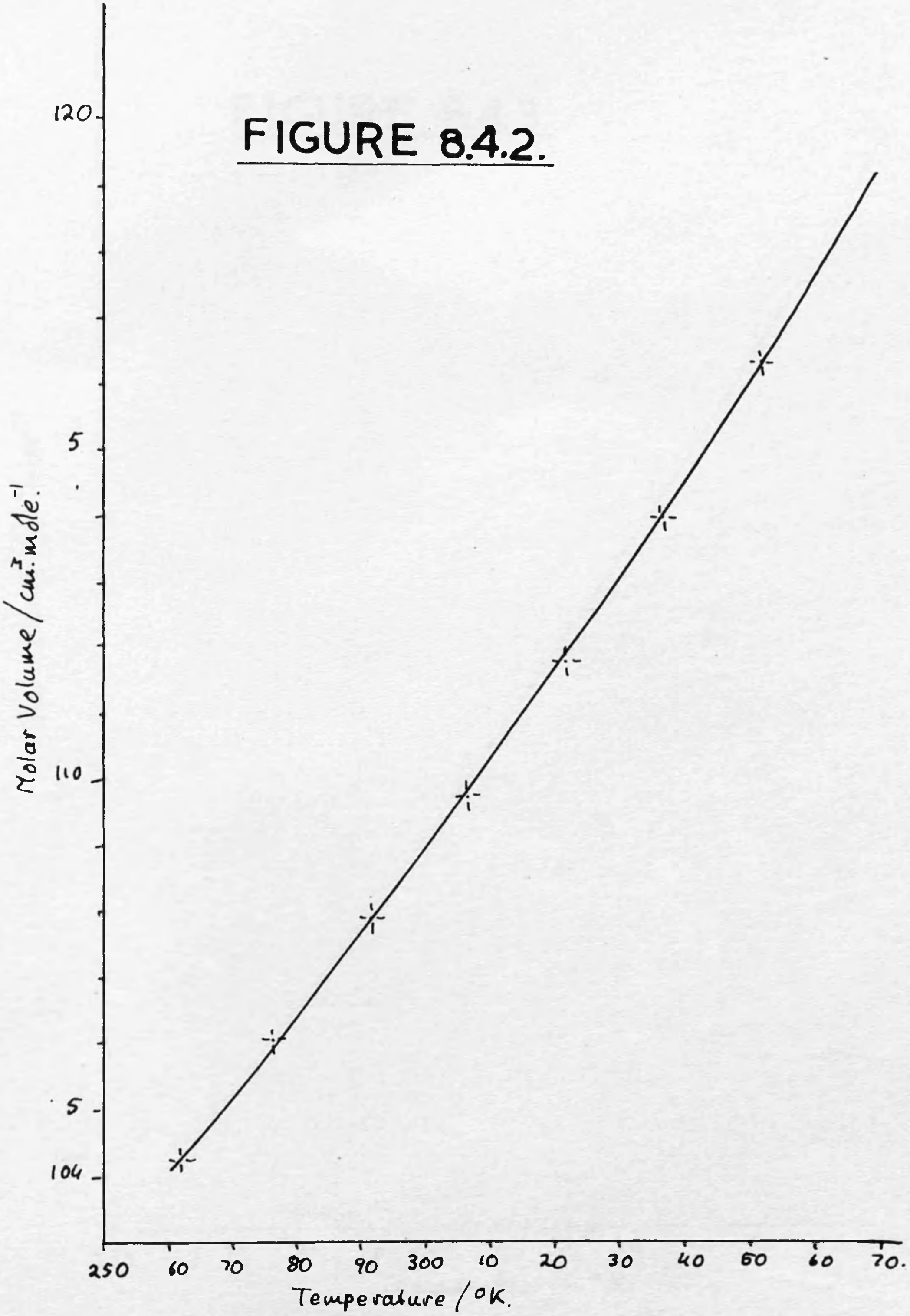
FIGURE 8.4.1.



SUPERPOSITION PLOT FOR CYCLOHEXANE-t-BUTYLCYCLOHEXANE.

$\mu = 1{\cdot}6624$ $\lambda = 1{\cdot}15$.

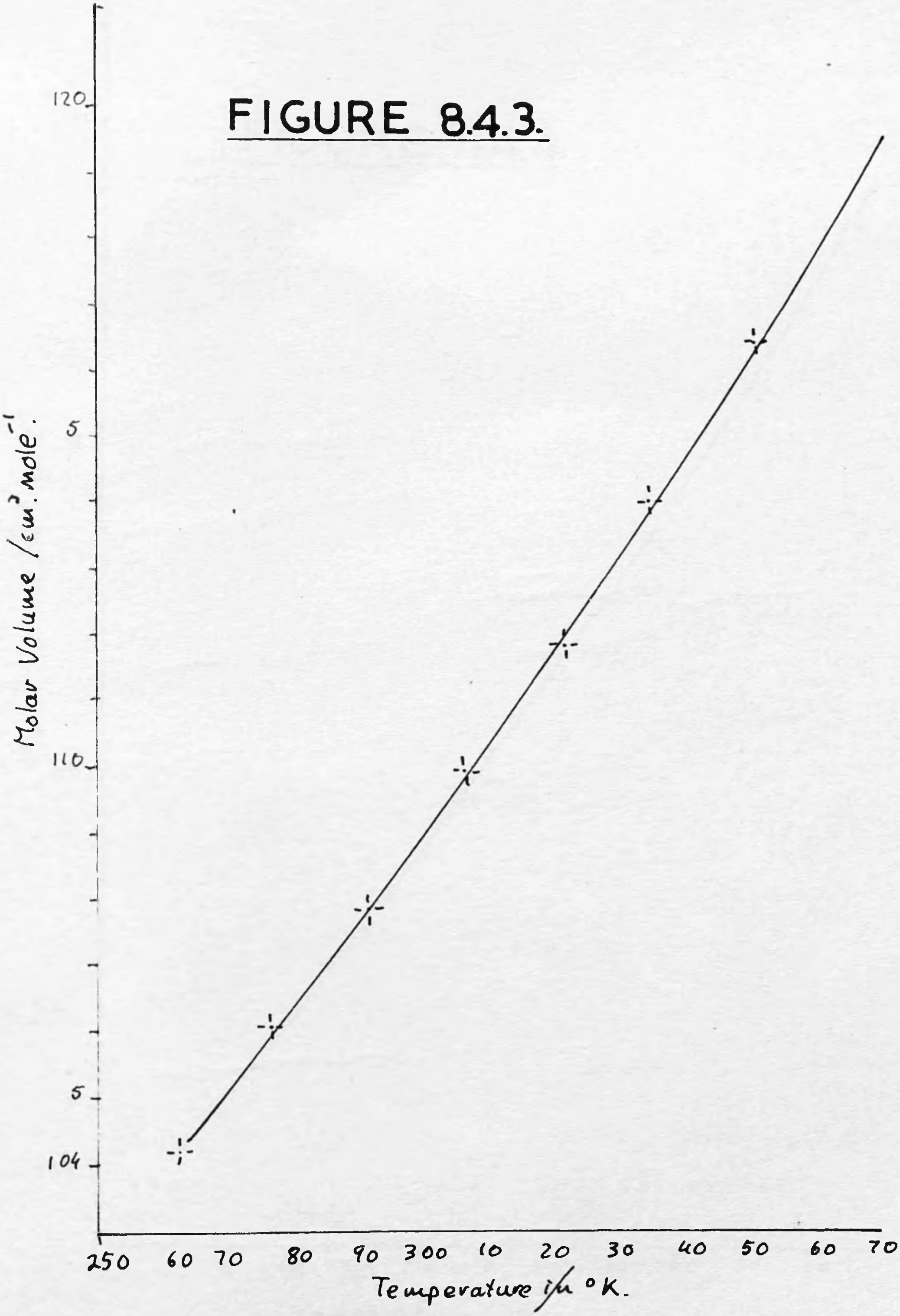
FIGURE 8.4.2.



SUPERPOSITION PLOT FOR CYCLOHEXANE + DICYCLOHEXYL.

$\mu = 1.891 \quad \lambda = 1.35.$

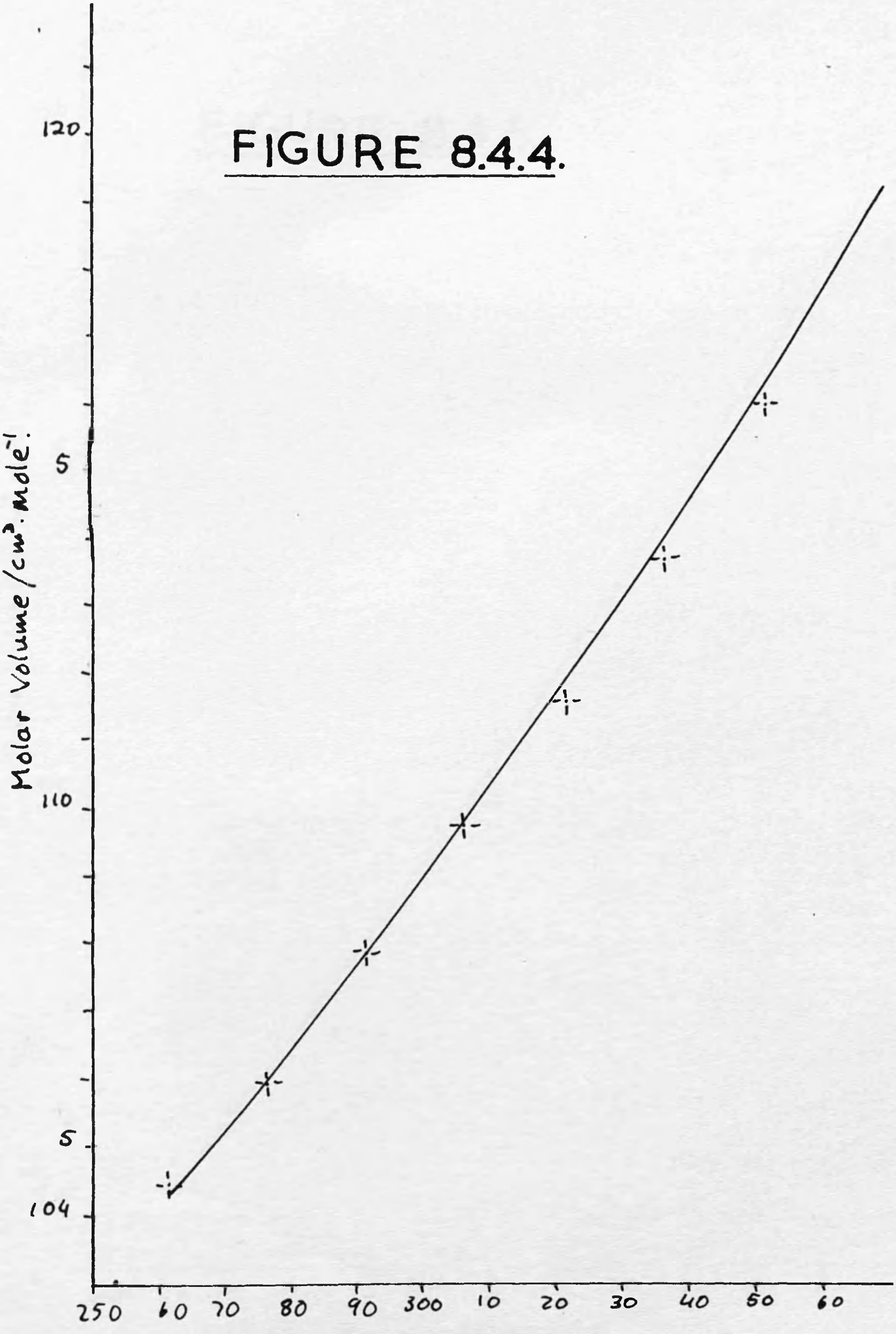
FIGURE 8.4.3.



SUPERPOSITION PLOT FOR CYCLOHEXANE + DICYCLOHEXYLMETHANE

$\mu = 2{\cdot}073_6$ $\lambda = 1{\cdot}35.$

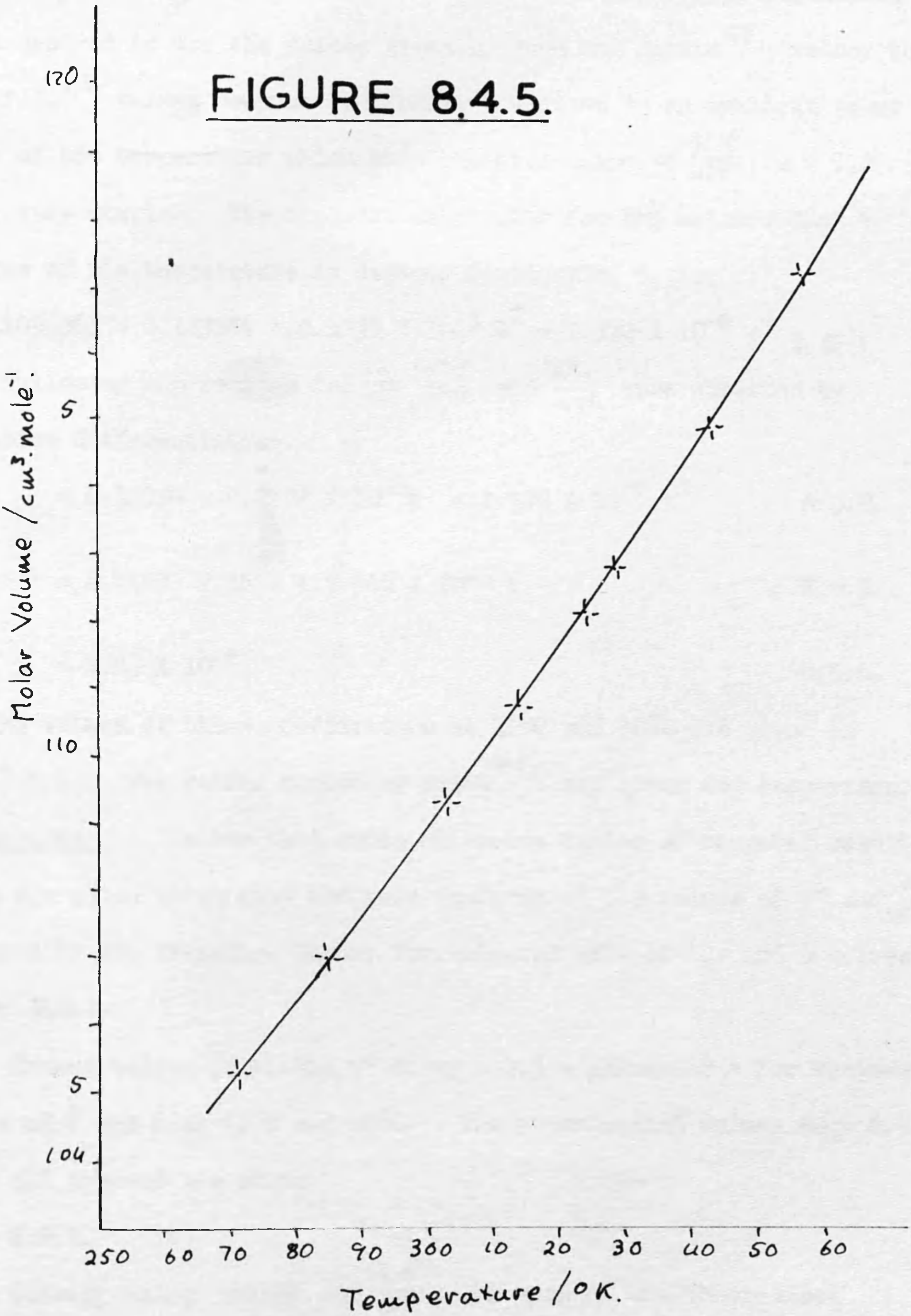
FIGURE 8.4.4.



SUPERPOSITION PLOT FOR CYCLOHEXANE +1,2-DICYCLOHEXYLETHANE

$\mu = 2.228$ $\lambda = 1.35$.

FIGURE 8.4.5.



SUPERPOSITION PLOT FOR CYCLOHEXANE + 1,3-DICYCLOHEXYLPROPANE.

$\mu = 2{\cdot}419 \quad \lambda = 1{\cdot}38$

terms v_1, $\frac{dv_1}{dT}$ etc. refer to its molar volume and temperature dependence. It was decided to use the values given by Wood and Austin[59] rather than the A.P.I.[113] values because the former are given in an explicit power series of the temperature which made the evaluation of $\frac{d^n v_1}{dT^n}$, n = 1, 2 and 3, very simple. The explicit expression for the molar volume v_1 in terms of the temperature in degrees Centigrade, t, is,

$$v_1 = 105.564 + 0.12386t + 0.1239 \times 10^{-3} t^2 + 1.310 \times 10^{-6} t^3 \qquad 8.5.1.$$

The following expressions for $\frac{dv_1}{dT}$, $\frac{d^2v_1}{dT^2}$ and $\frac{d^3v_1}{dT^3}$ were obtained by successive differentiation.

$$\frac{dv_1}{dT} = 0.12386 + 0.2478 \times 10^{-3}t + 3.930 \times 10^{-6} t^2 \qquad 8.5.2.$$

$$\frac{d^2v_1}{dT^2} = 0.2478 \times 10^{-3} + 7.860 \times 10^{-6} t \qquad 8.5.3.$$

$$\frac{d^3v_1}{dT^3} = 7.86 \times 10^{-6} \qquad 8.5.6.$$

The values of these coefficients at 20°C and 40°C are given in Table 8.5.1. The values quoted by Scott[47] are given for comparison.

8.6. Results. Rather than quote extensive tables of computer results, graphs are given which show the main features of the values of v^e and $\frac{dv^e}{dT}$ predicted by the Prigogine Theory for selected sets of θ, ρ and δ values.

Figure 8.6.1.

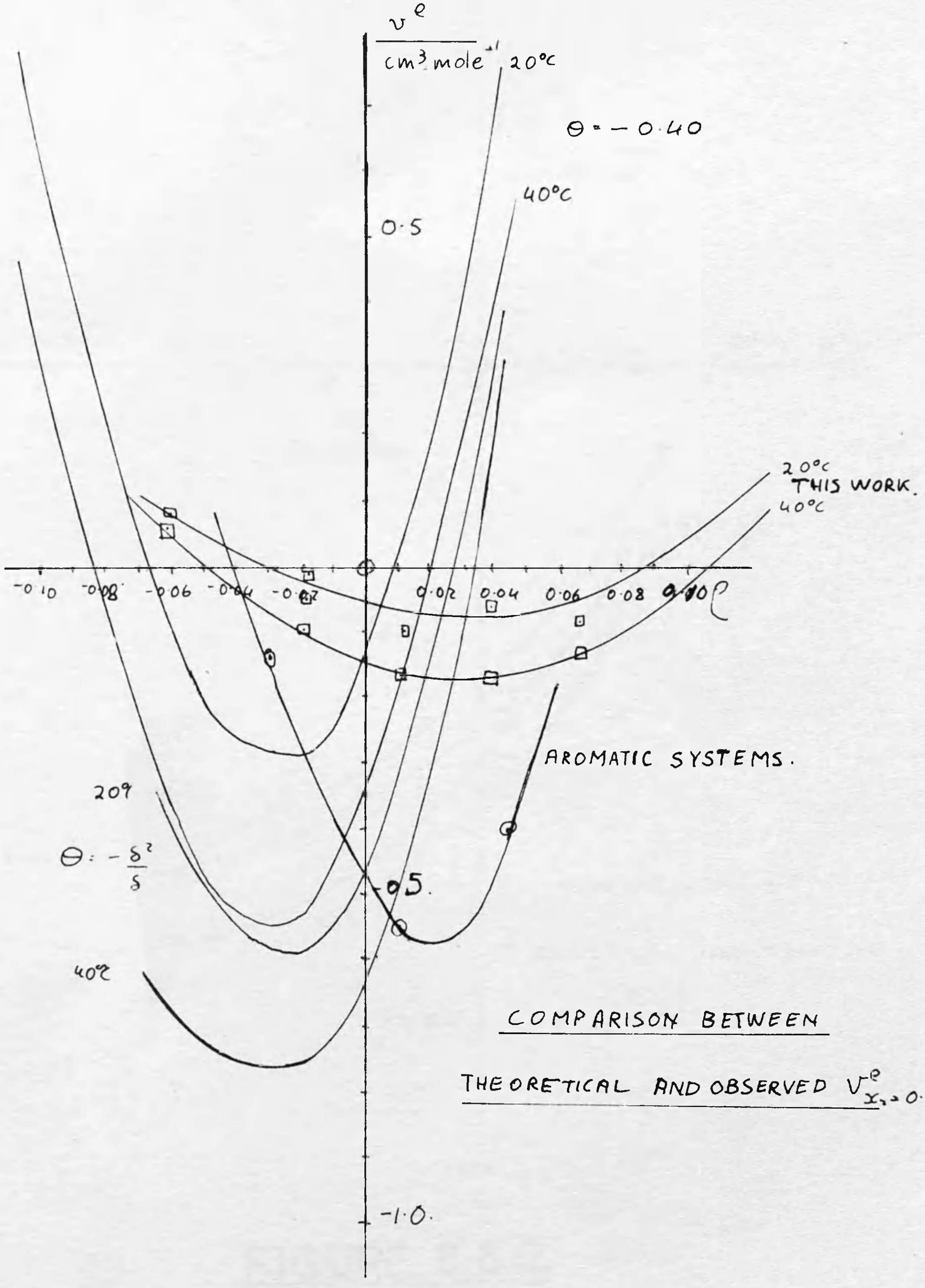
Excess volume of mixing, v^e at $x_2 = 0.5$ v. parameter ρ for various values of θ and δ at 20°C and 40°C. The experimental values at $x_2 = 0.5$ for all systems are shown.

Figure 8.6.2.

Corresponding values for $\frac{dv^e}{dT}$, the mean of the theoretical values at 20°C and 40°C are plotted to give fairest comparison with the experimental points.

Figure 8.6.3.

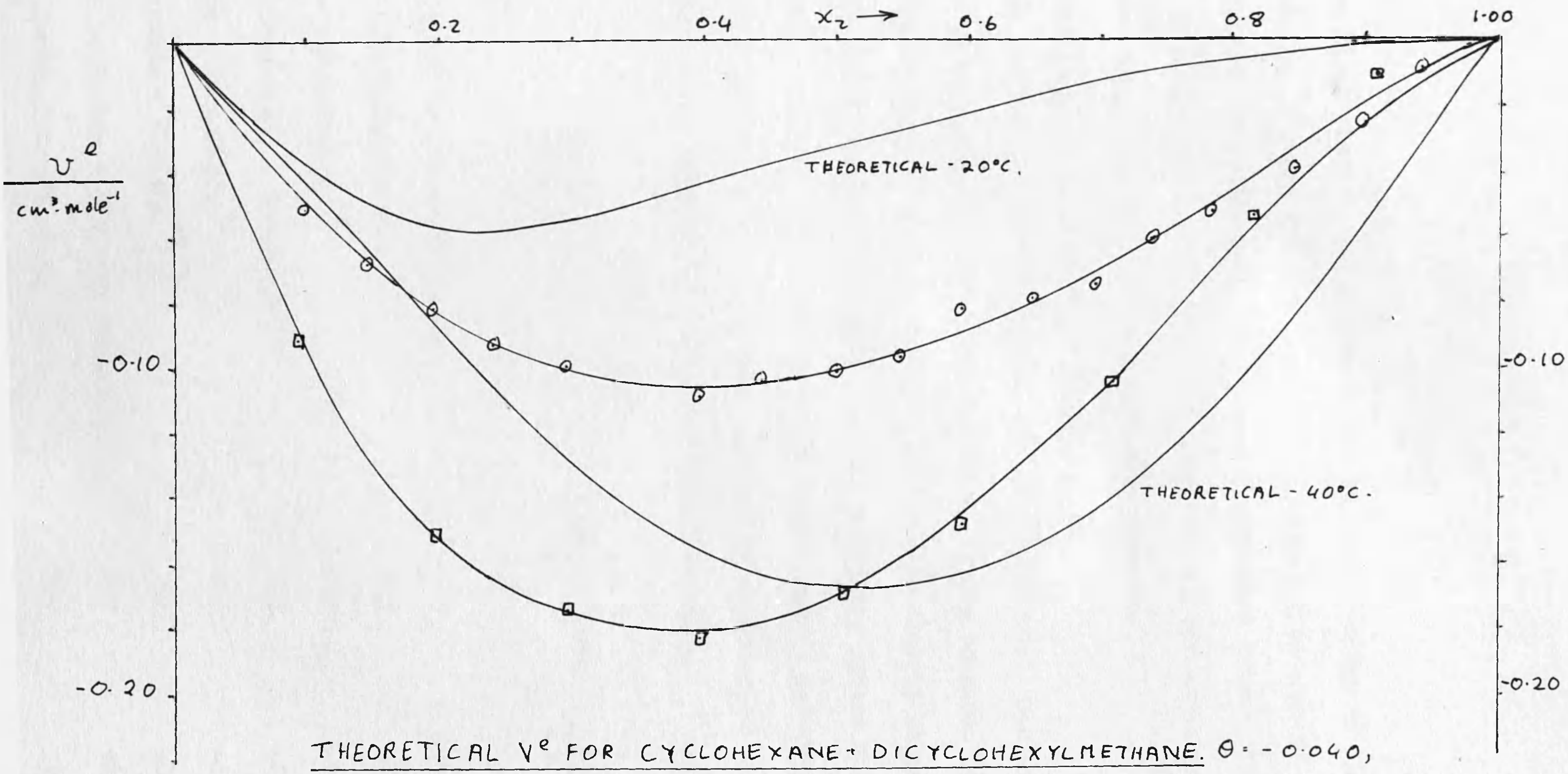
The excess volume of mixing, v^{θ} for cyclohexane and dicyclohexylmethane at 40°C, is plotted against x_2, the mole fraction of dicyclohexylmethane. The experimental and the theoretical points are given The value of θ is chosen to fit the experimental results at $x_2 = 0.5$.



COMPARISON BETWEEN THEORETICAL AND OBSERVED $V^e_{x_2=0.5}$

FIGURE 8.6.1.

FIGURE 8.6.3.



THEORETICAL V^e FOR CYCLOHEXANE + DICYCLOHEXYLMETHANE. $\theta = -0.040$, COMPARED WITH EXPERIMENTAL VALUES.

⊙ - 20°C ⊡ - 40°C.

Chapter 9.

Discussion.

9.1. Introduction.

In the final chapter, the measured and predicted values of the excess volume of mixing, v^e, and $\frac{dv^e}{dT}$ are discussed in relation to some of the factors involved. In particular, the extent of agreement between theory and experiment is analysed and various explanations for it are tentatively put forward. Some suggestions for further work are proposed.

9.2. Discussion of the Experimental Results.

9.2. Discussion of the Experimental Results.

One of the most striking features of the experimental results is the small order of magnitude of the excess volume of mixing compared to the total volume of the system, at a given composition. This is clearly shown in Table 9.2.1. which contains the values of the percentage excess volume of mixing, $100v^e \div (x_1v_1 + x_2v_2)$ for the system cyclohexane + 1,2-dicyclohexylethane at 40°C and for a number of other systems of mixtures of non-polar liquids. The values refer to $x_1 = x_2 = 0.5$ in all cases.

Table 9.2.1.

System	Temperature. T°K	$\frac{100v^e}{x_1v_1 + x_2v_2}$ %
Cyclohexane+1,2-dicyclohexylethane.	293	-0.04
Benzene + 1,2-diphenylethane.[116]	343	-0.21
n-Hexane + n-Hexadecane.[77]	293	-0.25
Carbon tetrachloride + Neopentane.[33]	273	-0.47
Cyclohexane + Neopentane.[33]	273	-1.00
Carbon Monoxide + Methane.[117, 63.]	91	-0.75
Carbon Tetrachloride + Silicone Tetrachloride.[72.]	298	+0.02
Methane + Carbon Tetrafluoride.[64]	107	2.10

The small magnitude of v^e, which for a given system is a measure of the departure from ideality, supports the initial belief that the set of systems chosen should be fairly amenable to theoretical treatment.

Almost all the v^e v. x_2 curves are non-symmetrical and are skewed towards low values of x_2. The minima in the curves are in the region $x_2 = 0.3$ to $x_2 = 0.4$. The position of the minimum is shifted towards higher values of x_2 at higher temperatures. When v^e is plotted against ϕ_2, the volume fraction of the second component, the resulting curves are more symmetrical, with minima in the neighbourhood of $\phi_2 = \phi_1 = 0.5$, corresponding to $x_2 = 0.33$. The unsymmetrical shape of the v^e v. x_2 curves is typical of mixtures of r-mers and is also shown by Marechal's measurements on aromatic monomer + dimer systems[116] and those of van der Waals and Desmyter on mixtures of normal hydrocarbons.[77]

The shift in the minima towards higher compositions as the temperature rises is less pronounced for v^e v. ϕ_2 plots than for v^e v. x_2 plots. This is partly due to the larger coefficient of thermal expansion of cyclohexane, $\alpha_c = 0.00124 \text{deg.}^{-1}$, compared to that of the dimer components, e.g. for dicyclohexylmethane, $\alpha_d = 0.000834 \text{deg.}^{-1}$ which causes the volume fraction of a solution of given mole fraction x to decrease as the temperature rises.

The v^e v. x_2 curves are mostly sigmoidal at high values of x_2. This is the region where the experimental uncertainty in v^e is a maximum.

The values of $\frac{dv^e}{dT}$ are small and when plotted against x_2, the curves show similar characteristics to the v^e v. x_2 curves, e.g. the minima are displaced towards small values of x_2. The constancy of $\frac{dv^e}{dT}$ with temperature was investigated for the system cyclohexane + dicyclohexyl by measuring v^e at 20°C, 30°C and 40°C. $\frac{dv^e}{dT}$ was found to be constant within experimental error over this temperature range.

The system cyclohexane + t-butylcyclohexane differs from the others in th

$\frac{dv^E}{dT}$ is zero within experimental error.

9.3. Discussion of Theoretical Results.

An important feature of the measured values of the interaction energy and separation parameters, δ and ρ, is the equality within experimental error, of the value of δ for each system except cyclohexane + t-butylcyclohex;hexane. Since δ is a measure of the difference between ε^*_{22} and ε^*_{11} and the latter is a constant for all systems, it follows that the value of ε^*_{22} must be very similar for each type of dimer molecule. This finding substantiates the initial hope that the set of systems chosen would display behaviour depending primarily on differences in size, as expressed in the ρ values, and less on the interaction energy differences, as expressed by the δ values. It has been stated previously that there is no simple way of calculating Θ for the type of system studied here, and the value used was chosen in a fairly arbitrary fashion. It was tacitly assumed that the value of Θ would tend to parallel the value of δ, as in the relationship $\Theta = -\delta^2 \div 8$ which is obtained from the geometrical mean rule. Since δ is constant for most systems, Θ was taken to be constant also.

The value of $\delta = 0.36$ was chosen as the average of the δ values for the systems not containing t-butylcyclohexane, and lay within the experimental uncertainty limits of these systems. It has been suggested by Professor R.L. Scott[118] that the system cyclohexane + t-butylcyclohexane is not a suitable system to compare with the other monomer-dimer systems because of the presence of the methyl groups in t-butylcyclohexane. A confirmation of this view is the anomalous value of $\delta = 0.15$ for this system compared to the mean value $\bar{\delta} = 0.36$

for the other systems. A simple test of the effect of the presence of methyl groups in a molecule would be the measurement of δ for such systems as cyclohexane + 1,1-dicyclohexylethane, 1,2-dicyclohexylpropane of 2,2-dicyclohexylpropane.

The principal object of the present research was to test Prigogine's prediction that the excess volumes of mixing of a set of systems of r-mer mixtures with constant δ and θ values, should show minima when the chain length of one component was approximately an integral multiple of that of the other component. In the terminology used in this work, this prediction may be rephrased to state that the excess volume of mixing should show a minimum for systems of monomer-dimer mixtures near values of ρ equal to zero. This prediction was based upon the inspection of theoretically derived curves of v^e v. ρ for constant values of δ and θ. The theoretical results were most conveniently compared with the experimental values in the present work, using the same type of v^e v. ρ plots.

The most noticeable feature of the theoretical results is the great sensitivity of v^e to θ and to a lesser extent to z, the number of nearest neighbours of a monomer molecule in the liquid. A discussion of the significan of the θ values is given later.

Many calculations in the field of liquid mixtures have been based on a choice of z = 12. Using this value, and reasonable values of θ, it was found that the predicted values of v^e were much larger than the observed values although the correct sign was given. Closer agreement was obtained using z = 6 and this was therefore used throughout, the remaining calculations. The factors q and δ depend on the value of z chosen.

The use of values of $z < 12$ may be shown to be more reasonable for simple considerations of the molecular structure of liquids. The value $z = 12$ is the maximum possible co-ordination number for a close-packed structure composed of spheres. It is unlikely that, in a liquid, whose most obvious characteristic at molecular level is the presence of considerable thermal motion which destroys long-range order, that this maximum co-ordination number obtains. It is more likely that a lower average value is correct. This conclusion is also reached by Hildebrand[31] who suggests that $z = 8 \rightarrow 9$ is more suitable. Paterson finds that Prigogine's theory of polymer solutions reproduces his experimental measurements when the value of z is taken between three and four.[119] It is of interest that Prigogine, Trappeniers and Mathot, in a discussion of the extension of the cell theory to r-mer mixtures, find agreement between predicted and observed g^e and h^e values using $z = 12$, and without any explanation use $z = 6$ to find better agreement between theory and experiment for the value of v^e.[56]

9.4. The Comparison between Theory and Experiment.

The value of θ which is used in the expression 3.5.13., is largely arbitrary although there are fairly narrow limits within which it must fall. No experimental information is available which allows θ to be calculated and so the value obtained from the geometrical mean rule, $\theta = -\delta^2 \div 8$ was tried first. In this case $\theta = -0.0128$.

The v^e predicted using this value of θ was very much larger than the measured value and it was decided to force agreement between the predicted and observed values of v^e for the system cyclohexane + dicyclohexyl methane at 40°C. This system was chosen as being near the middle of the chosen set. The value of θ found was -0.040.

Since this value is greater than that predicted from $\theta = \frac{-\delta^2}{8}$, it follows that the assumption of an arithmetic mean rule for ε_{12}^{*}, which results in $\theta = 0$, is even worse than the assumption of the geometric mean rule.

It is not surprising that the best value of θ is not close to the geometric mean value since the molecules in the systems studied are neither truly spherical nor monoatomic which are the conditions for which this should apply.

The main points of interest arising from a comparison between the theoretical and experimental values of v^e, using $\theta = -0.040$, are discussed separately.

1. The theory predicts values of v^e which are of the same magnitude and sign as the experimental values although the quantitative agreement is less satisfactory.

2. The expected minimum in v^e, when plotted against ρ, is observed. The magnitude of the theoretical minimum is greater than the observed minimum by a factor of approximately three and its position is displaced to a negative value of ρ compared to the positive value observed.

The experimental values at $x_2 = 0.5$, and 40°C fall on a smooth curve but those points at 20°C do not. The values of v^e at 20°C for the systems cyclohexane + dicyclohexylmethane and cyclohexane + 1,2-dicyclohexylethane are somewhat anomalous but there is no doubt about the values shown since they were both checked by repeated measurement. Both sets of measurements agreed within experimental error.

3. The values of $\frac{dv^e}{dT}$ predicted by the theory are of the correct order of magnitude and sign but are too large by a factor of about two.

4. The observed minimum in $\frac{dv^e}{dT}$ is reproduced by the theory, but its position is grossly misestimated. It is noticeable that the use of different values

of v_1, $\frac{dv_1}{dT}$ etc. produces different values of $\frac{dv^e}{dT}$ at 20°C and 40°C which appears to be in contradiction with the experimental results for the system cyclohexane + dicyclohexyl.

The smooth curve which can be drawn through the values of $\frac{dv^e}{dT}$ is broken only by the value for the system cyclohexane + dicyclohexylmethane. It is clear then that in the v^e v. ρ curves, greater weight can be attached to the cyclohexane + 1,2-dicyclohexylethane value at 20°C, since $\frac{dv^e}{dT}$ for this system is in better accord with $\frac{dv^e}{dT}$ for the other systems of the set.

No good reason is apparent to explain the behaviour of the cyclohexane + dicyclohexylmethane system. The trend of the physical properties from dicyclohexyl to 1,3-dicyclohexylpropane is generally undisturbed, e.g. the boiling-points at 760mm. Hg, are 233°C, 252°C, 272°C, 292°C, the only slight exception being in the molar volumes. At 25°C, for example, the molar volumes are 188.5cm^3, 206.5cm^3, 222.4cm^3, 239.8cm^3. This slight irregularity is probably insignificant and provides no explanation for the observed v^e behaviour.

5. When the curve of v^e v. x_2 is drawn for cyclohexane + dicyclohexylmethane at 40°C, using $\Theta = -0.040$, the observed shape of the curves is not well reproduced although the dissymmetry is in the correct direction.

6. It is of interest to plot the values of v^e for the aromatic equivalents of some of the systems. Table 9.4.1. contains the available information on such systems.

Table 9.4.1.

System	Temperature.	δ	ρ.	v^e
	$T^\circ C$	z = 6		$cm^3 mole^{-1}$.
Benzene + diphenyl.[116]	70	0.42	-0.025	-0.14
Benzene + diphenylmethane.[19]	70	0.40	+0.010	-0.6
Benzene + 1,2-diphenylethane.[116]	70	0.60	+0.046	-0.4.
		±0.04	±0.05	

The v^e values are plotted in Figure 8.6.1. along with those for the alicyclic systems studied in this work. A minimum is also found. No further conclusion can be derived from these results since the δ values are very different. A comparison with the theory could be obtained by calculating v^e using the values of v_1, $\frac{dv_1}{dT}$ etc. for liquid argon at the same reduced temperature and then multiplying by the ratio of critical volumes of benzene and argon. This procedure would be occasioned by the non-obeyance by benzene of the Principle of Corresponding States.

9.5. Discussion of the Agreement Found.

It is easy to suggest reasons why the theoretical and experimentally determined values of v^e do not agree more satisfactorily, but it is difficult to assess the weight which should be given to any one reason. Nevertheless, the following suggestions are tentatively put forward to explain the discrepancies.

1. The expression 3.5.13. which was used to calculate v^e and $\frac{dv^e}{dT}$ in terms of the physical properties of the reference substance, is in the form of a series as far as the second derivative of v_1 with respect to T, i.e. $\frac{d^2v}{dT^2}$. It is found that the terms in equation 3.5.13. do not converge rapidly and it is possible that a more complete theory would include further terms

including $\frac{d^3 v}{dT^3}$ etc. These would however be increasingly difficult to evaluate.

2. The pure components are assumed to obey the same Principle of Corresponding states. The good superposition of the v(T) v. T curves suggest that in the present case, this is a valid assumption but no test of the further assumption, that the mixture also obeys this same Principle of Corresponding States is as yet possible, and this may be a source of error.

3. The use of unsymmetrical interaction parameters, θ, δ and ρ, has been criticized by Scott,[118] who in his Corresponding States treatment of mixtures of molecules of nearly equal size, uses interaction parameters which are symmetrical in both components. It is a feature of the present work that the values of δ and ρ, which are used to calculate volume changes, are themselves derived from measurements of volume and not some unrelated property such as latent heat and this probably lessens the objection.

4. In the Prigogine treatment, the assumption of random mixing is used. Brown,[44] who has investigated the properties of random mixtures, suggests that this assumption becomes questionable in the case of mixtures of molecules of unequal size. It is possible that the agreement between theory and experiment could be improved if the effects of non-random mixing were introduced.

5. The uncertainty in the value of θ to be used could be minimized by determining the value of ε^{*}_{12} for each system experimentally, e.g. from the virial coefficients of gaseous mixutres or diffusion, measurement of diffusion. The theory would be tested more fairly using values of θ obtained in this way.

6. The effects of non-central forces could be investigated using a Lennard-Jones (28-7) potential which gives better agreement with some of the properties of globular molecules.[20]

7. A more exact value for s could be found e.g. from X-ray work and this would further lessen uncertainties in the theory.

9.6. Suggestions for Further Work.

Suggestions for further work include the following;

1. The determination of v^e at other temperatures so as to investigate the variation of $\frac{dv^e}{dT}$ with temperature suggested by the theoretical results.
2. The determination of v^e for the systems cyclohexane + dicyclohexylether, cyclohexane + cyclohexylmethylcyclohexyl ether. Since ethers are very similar to hydrocarbons, systems could be expected to have δ values similar to the pure hydrocarbonsystems and ρ values intermediate between those of the systems investigated. The shape of the v^e v. ρ curves could then be investigated more exactly.
3. The measurement of v^e for systems containing methyl groups, e.g. cyclohexane + 2,2-dicyclohexylpropane.. The effect of the methyl groups in the dimer molecule could be thus investigated.

9.7. Conclusions.

The predictions of the Prigogine, Average-Potential, Corresponding States theory of Polymer solutions were not intended to provide numerically exact values for the excess functions, but it was hoped that they would show semi-quantitative agreement with experimentally measured values.

It is clear that in the present work, this hope has been vindicated since the predicted values of $\frac{dv^e}{dT}$ and v^e are in fair quantitative agreement with the measured values both in sign and magnitude.

The prediction of the minimum behaviour of v^e for systems of monomor-r-mer mixtures has been experimentally verified. Since the verification of this prediction was stated by Prigogine to be a sensitive test of the whole theory, it may be claimed that the present work has provided a confirmation of the basic assumptions of the theory.

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PART II.

The Preparation and Properties of Aluminium Hydride Etherate.

The Preparation and Properties of Unsolvated Aluminium Hydride.

1. Introduction.

The binary compounds of hydrogen may be classified into three principal categories according to broad differences in their structures, physical properties and chemical behaviour.[1]

1. **The Ionic Hydrides.** In combination with strongly electropositive elements such as the alkali or alkaline earth metals, hydrogen appears to be strongly electronegative in character and exists as the negatively charged hydride ion H^-. The hydrides of these metals e.g. NaH are very similar to the corresponding ionic halides, and they display high melting points, high heats of sublimation, high degrees of thermal stability and are conductors of electricity in the fused state.

2. **The Transitional Metal Hydrides.** The transitional metal hydrides are the hydrides of the elements lying in the centre of the Periodic Table and in which the incomplete electron shells underlying the valency electron shells become progressively occupied and expanded with increasing atomic numbers. These compounds are considered as a group largely from convenience, despite wide variations in their nature and properties. Many comprise little more than molecular hydrogen e.g. palladium hydride, physically adsorbed in defects in the structure of the metal. Others are formally analogous to alloys in that the hydrogen behaves like a metal. A few are similar to the ionic hydrides of the first group.

3. **The Covalent Hydrides.** The covalent hydrides form the majority of the known binary hydrides and comprise those hydrides in which the chemical bonding is primarily of the non-polar, electron-sharing type. There is considerable variation in the chemical properties of this class of hydrides as can be seen

by hydrogen fluoride and methane, but they have much in common in their physical properties. They are in many cases gases or volatile liquids, and only in a few cases are obtained as solids.

There are a number of hydrides which lie outwith the above classification and these may be termed border-line hydrides, examples are the hydrides of copper and zinc.

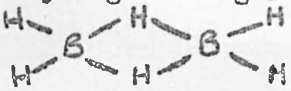
The hydrides of group 111 elements, e.g. boron, aluminium and gallium are classed as covalent hydrides. Although each of these elements is more electropositive than hydrogen, the actual differences in electronegativity are small, and the small size and high charge of the atoms causes the bonding in their compounds to be largely covalent. The heavier elements of group 111, indium and thallium form unstable ill-defined hydrides which fall into the border line class.

The group 111 hydrides are unique in several respects. They are extremely unstable substances in the main, and are extremely prone to decomposition through or oxidation. The large heat of combustion in the latter case has led to their use as rocket fuels. The boron hydrides have been of particular interest in this regard. The most important and difficult~~ly~~ to explain~~ed~~ features of the group 111 hydrides, are the nature of the chemical bonding and the valency relationships which they display.

2. The Structure of Aluminium Hydride.

The difficulty in explaining the chemical bonding in the hydrides of the first three group 111 elements lies in the fact that those compounds generally contain fewer electrons than are required for normal, two-electron, covalent bonds between all the atoms in the molecule. The term "electron-deficient" has been applied to this class of compounds.

The compound which stimulated most interest in the subject of electron-deficient hydrides is diborane. B_2H_6. The number of valency electrons available in this molecule is twelve. It can be seen from the known structure that this number is insufficient to supply normal two-electron covalent bonds between all the atoms in the molecule. The presently accepted explanation is that the "odd" pair of protons form "hydrogen bridges" between the boron atoms.[1]



The present work was mainly concerned with aluminium hydride, AlH_3, and a short description is given of the various suggestions which have been made to explain its structure.

The first report of the preparation of aluminium hydride was made by O. Stecker and E. Wiberg,[2] who obtained a non-volatile, seemingly polymeric material, and some volatile derivatives of monomeric aluminium hydride by the action of the electric discharge upon alkyl aluminium compounds. The proposed structure was that of a linear polymer in which the aluminium atoms are connected by single hydrogen bridges.

This preparation prompted speculation on the possible structure and bonding in the polymer of the electron deficient units (AlH_3). Thus H.C.Longuet-Higgins[3] suggested that polymerisation took place in two dimensions such that:

1. The hydrogen atoms form bridges in pairs between the aluminium atoms, with each aluminium atom joined octahedrally to six hydrogen atoms.
2. All the Al.....H bonds in the giant molecule are crystallographically equivalent.
3. The aluminium atoms are arranged in two-dimensional layers at the vertices of a hexagonal tesselation.

This structure embodies the concept of the "protonated double-bond" which had been introduced earlier by K.S.Pitzer[4] to explain the wide range of structures of the many known boron hydrides. A similar structure was shown to be possible without using the "protonated double-bond" concept and using instead a set of octahedrally disposed Sp^2d^3 hybridized orbitals. Essentially the same structure was proposed by E. Wiberg[5] but the nature of the bonding present was not discussed.

A further approach to the structural problem was given by Rundle[6.] who extended the principle of bond delocalization by suggesting that if one atom, usually a metal atom, with more low energy orbitals than valency electrons, combined with atoms containing unshared electron pairs, then bond delocalization would occur.

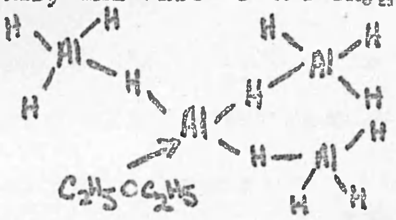
All of the suggested structures described above are almost wholly unsupported by experimental evidence, except that the involatility of the materials suggests a polymeric structure.

Attempts have been made to determine the structure using X-ray methods,[7] but although an unusual and characteristic diffraction pattern was obtained which suggested that a crystalline rather than an amorphous form exists, the studies helped little towards resolving the molecular configuration.

The involatility of the substance and the difficulty of preparing it in thin films, preclude the application of electron-diffraction techniques.

The infra-red spectra of various etherates and aminates of aluminium hydride have been described.[8.] Although the previously suggested pyramidal symmetry of the mono-addition compounds was confirmed, little information on the pure hydride was forthcoming.

The most useful structural studies on aluminium hydride are those reported by R.F.Nickerson,[9.] in which the etherates of aluminium hydride were examined by nuclear spin resonance techniques. The etherates of aluminium hydride and deuteride obtained from several preparative methods were studied and a structure for the etherate was deduced. In this structure a central aluminium atom is attached tetrahedrally through hydrogen bridges to three other aluminium atoms which are each bonded with three hydrogen atoms, and also to the oxygen of an ether molecule by a normal coordinate bond.



The formula of the unit is given as (AlH_3)$_4$$Et_2O$. This structure is o very different from any previously suggested but it has the merit of being supported by quantitative evidence.

3. General Methods of Preparation of Aluminium Hydride.

The following is a classification of some of the diverse reactions in which aluminium hydride has been reported.

1. The first method reported involved the decomposition of alkyl aluminium compounds in an electric discharge.[2]

$$Al(Me)_3 + 3/2\,H_2 \longrightarrow AlH_3 + 3CH_4.$$

2. The availability of the complex hydride, lithium aluminium hydride $LiAlH_4$, greatly facilitated the preparation.[10,11] The treatment of aluminium chloride $AlCl_3$ in ether solution with a solution of lithium aluminium hydride yielded a solution of aluminium hydride and a precipitate of lithium chloride.

$$3\,LiAlH_4 + AlCl_3 \longrightarrow 3LiCl + 4\,AlH_3$$

The aluminium hydride rapidly polymerizes to give a polymeric, insoluble etherate. The polymerization can be reversed or prevented by the addition of an additional mole of aluminium trichloride solution which causes the formation of the stable compound $AlH_3.AlCl_3$.[11,12] A similar type of stabilization is noted by the addition of tertiary amines.

3. The preparation of non-solvated aluminium hydride was reported by T.R.P.Gibb et al.[13] An ethereal solution of aluminium hydride was poured into

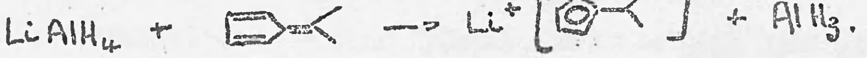
a large excess of non-solvating hydride such as n-pentane and the precipitate of hydride was separated and rendered free of n-pentane by evacuation.

A number of other reactions are described in the literature in which aluminium hydride is said to be formed. A survey of these was made with a view to deciding which would be most useful as routes to unsolvated aluminium hydride. The following are among the most promising,

a. The treatment of trimethylamine hydrochloride with lithium aluminium hydride to form the adduct $AlH_3.NMe_3$ which may be separated from the solvent.[11,14] It has been suggested that $AlH_3.NMe_3$ should break down on thermal decomposition to form AlH_3.[14]

$$LiAlH_4 + NMe_3HCl \rightarrow LiCl + H_2 + AlH_3.NMe_3.$$

b. The treatment of dimethylfulvene with one molar equivalent of lithium aluminium hydride gives the following reaction,[16,17]



The reaction only takes place in the presence of ether or some other solvent suitable for hydride ion transfer.

c. The decomposition of metal aluminium hydrides is fairly common. If some method of separating the resulting metal and AlH_3 could be found, this reaction would be a useful source of aluminium hydride.[18,19]

$$2In(AlH_4)_3 \xrightarrow{-40°c} 2In + 6AlH_3 + 3H_2$$

$$Sn(AlH_4)_4 \longrightarrow Sn(AlH_4)_2 + 2AlH_3 + H_2$$
$$\hookrightarrow Sn + 2AlH_3 + H_2.$$

d. The decomposition of aluminium alkyl compounds. The preparation of solvent free beryllium hydride has been ~~prepared~~ described by G.E.Coates and F.Glockling,[20] by the action of heat upon di-t-butyl beryllium. A hydride of 96 %purity could be obtained. These authors note that substitution of hydrogen by methyl groups causes a progressive decrease in thermal stability in the order, Me_2Be, $(MeCH_2)_2Be$, $(Me_2CH)_2Be$, $(Me_3C)_2Be$.[21] The decomposition of the last compound gives mainly isobutene and beryllium hydride retaining some t-butyl groups.

$$Be(t\text{-}Bu)_2 \longrightarrow BeH_2 + 2CH_2{=}CH(CH_3)_2$$

The last reaction was considered to be of most interest and it was decided to attempt the preparation of tri-t-butyl aluminium hydride with a view to studying the results of the decomposition.

4. The Aims of the Research.

Initially the object of the research was to study aluminium hydride in a systematic fashion, with emphasis on its thermochemistry and its general reactivity. In fact, the period of time available was barely sufficient to cover the first step of the programme, which was the perfecting of a method of preparation of ether-free aluminium hydride, and the work described is confined to this aspect.

The importance of obtaining ether-free hydride was partly due to its potential value as a rocket fuel. The advantages of using aluminium hydride as a rocket propellant include the following,

1. The process of combustion of AlH_3 is highly exothermic as in the case of the related boron hydrides which have been used as rocket fuels.

2. The combustion product, Al_2O_3. is more refractory and thermodynamically stable than the boron oxides produced by the boron hydrides. The process of combustion is improved by the higher temperatures and increased exhaust velocities which are possible.

3. The boron hydrides, being liquids are less easy to work with than aluminium hydride which is a solid. The use of solid propellant rockets reduces the pre-

operational period of a rocket since only the oxidant need be loaded immediately before take-off.

It is found that aluminium bdyride is a very reactive substance. It reacts vigorously, and in some cases explosively with oxygen and water and it was thought that the presence of ether in the solid as normally prepared, was responsible for this. Accordingly it was decided, as a first step in the full programme, to try to prepare solvent-free or unetherated aluminium hydride.

The methods already described in the literature were re-investigated in order to test the validity of the claims made by the workers concerned and to explore the possibilities of improvement.

The most promising of the methods suggested by a literature survey of all the reactions in which aluminium hydride was reported, involved the preparation of tri-t-butyl aluminium and its subsecuent thermal degradation to aluminium hydride. It was decided to study this reaction.

The results of the work were that the previous methods of preparing aluminium hydride etherate were repeated and similar results to those in the literature were obtained. The method, supposingly producing non-etherated material, was investigated but could not be repeated. The new method of obtaining aluminium hydride by decomposition of tri-t-butyl aluminium could not be tested since the alkyl aluminium compound could not be prepared.

5. Experimental.

Apparatus. The materials used inthis investigation were mainly very sensitive to attack from atmospheric oxygen and water, particularly the latter, and in order to protect them from attack the following techniques were employed.

All manipulations involving water sensitive material were performed in a glove box in an atmosphere of dry nitrogen. This was also equiped to permit weighing and vacuum operations to be carried out in protected conditions.

All reactions were carried out in reaction flasks under dry nitrogen.

Materials.

Lithium Aluminium Hydride. The material used was the commercial grade supplied by Metal Hydrides Inc; although it was stated to have a purity greater than 95 %, analysis showed that the purity was only 92 % when fresh and even this decreased with usage.

Purification was carried out by ether extraction of the crude material and subsequent filtration and vacuum evaporation of the ethereal solution.

The apparatus for the Soxhlet extraction of lithium aluminium hydride is shown in Figure 1. Dry ether was obtained by distilling the 'anaesthetic' grade material from crude lithium aluminium hydride in flask A into flask B under dry nitrogen.

Extraction under reflux was carried out for two days until sufficient hydride (10g) had been extracted. The cool solution was then filtered through a No. 3 sintered glass filter D under pressure of dry nitrogen into a collecting vessel C. This was transferred into a dry box for evaporation to dryness under vacuum at room temperature.

Leakage and sticking in the conical joints of the apparatus were minimized by fitting them with Teflon sleeves, and all outlets to the atmosphere were protected with silica gel drying tubes.

The white, crystalline solid had a purity of 99.1 based on Al determination, Some samples which were not evacuated for a sufficiently long time showed lower hydride content, the remainder being ether. These were suitable for use in the preparation of aluminium hydride without further treatment.

Aluminium Chloride. This was the anhydrous grade supplied by Hopkins and Williams Ltd. It was assumed to have a purity of 95 %, the impurities (e.g. Al_2O_3, $Al(OH)_3$) being insoluble in ether, and it was used without further

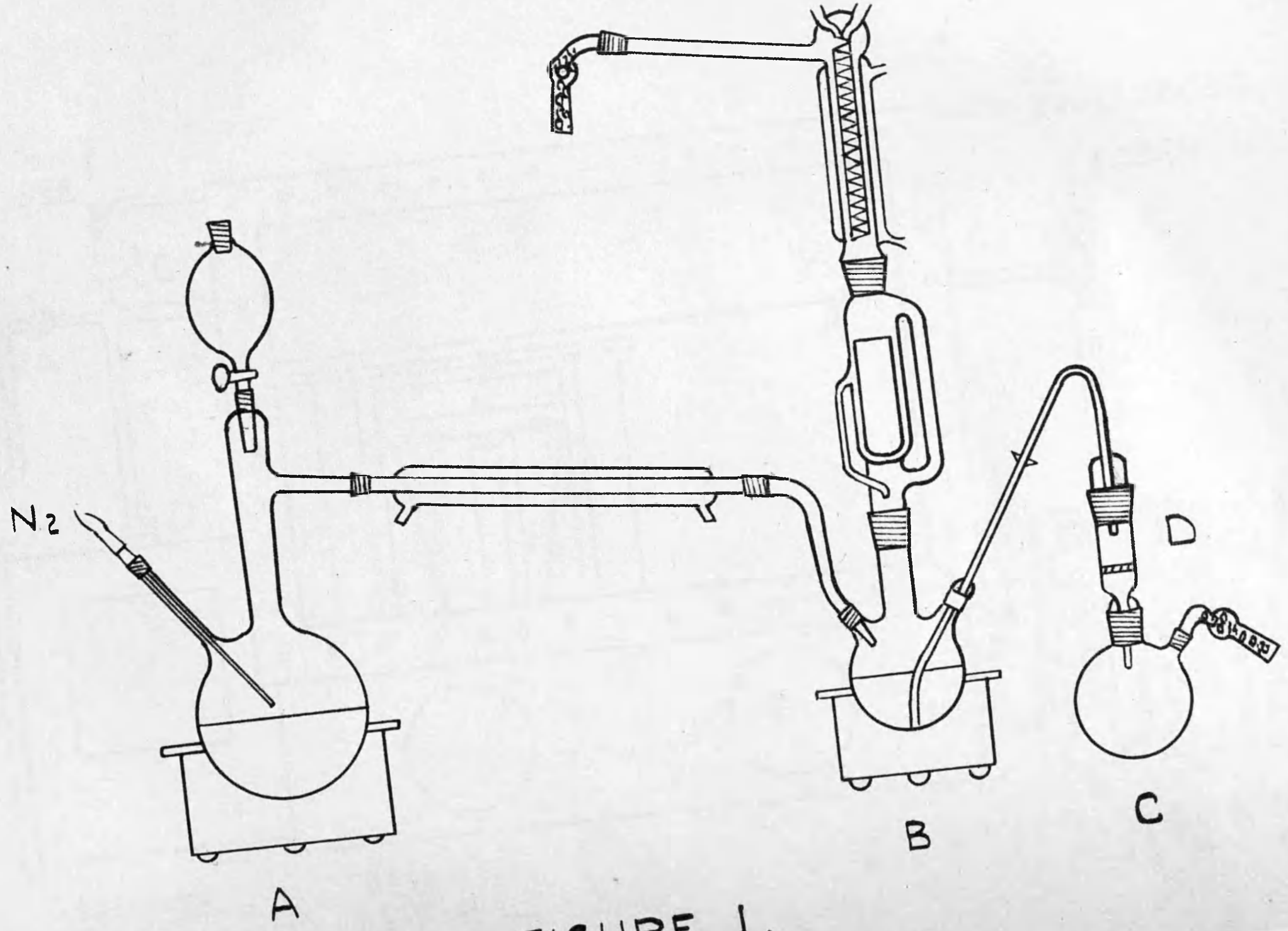


FIGURE I.

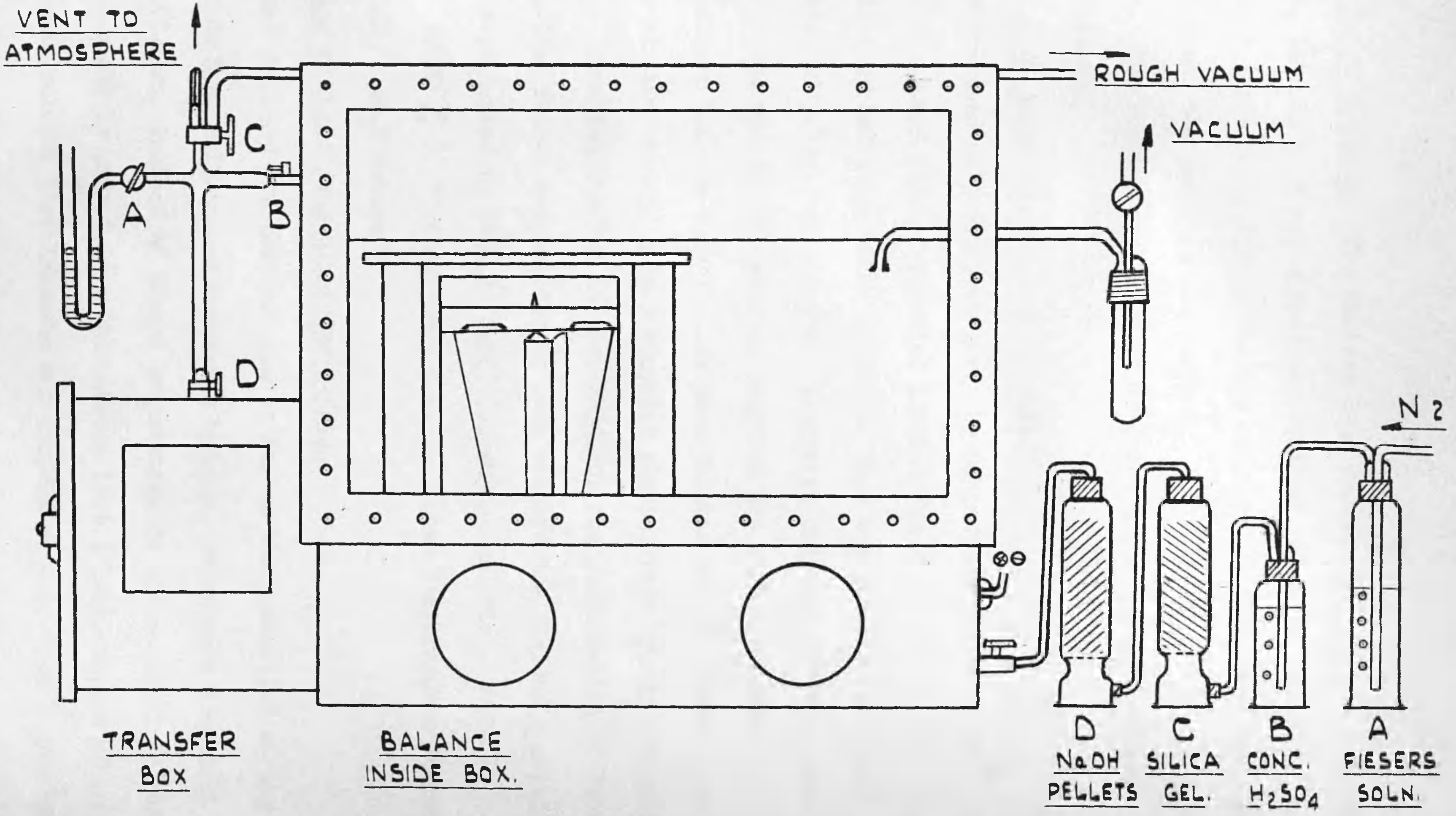

VENT TO ATMOSPHERE
ROUGH VACUUM
VACUUM
A
B
C
D
N 2
TRANSFER BOX
BALANCE INSIDE BOX.
D
NaOH PELLETS
C
SILICA GEL.
B
CONC. H_2SO_4
A
FIESERS SOLN.

FIGURE 2.

purification.

Tertiary Butyl Chloride. The British Drug Houses Ltd. product was redistilled (b.p. 51°C, lit. 51°C.) and stored over calcium chloride. Initially samples were stored over Linde Molecular sieves but catalytic breakdown of the alkyl halide occurred and the practice was stopped.

Magnesium. The Hopkins and Williams Grignard grade was used without further purification.

The Preparation of Aluminium Hydride Etherate.

The procedure used followed that given by Schlesinger and Finholt.[10] In a typical preparation 3.19g. of purified lithium aluminium hydride was dissolved in 100cm^3. ether by refluxing under nitrogen. When the solution was clear and cool, a solution of 3.73g. of anhydrous aluminium chloride (27.93m. moles) in 25cm^3. ether was added. The ensuing reaction was vigorous but of short duration, insoluble lithium chloride was precipitated and was removed by filtering the mixture through a No.3 sintered glass filter by dry nitrogen pressure in an apparatus similar to that used for the purification of lithium aluminium hydride. Vacuum evaporation at room temperature yielded a solid which may be represented as $(AlH_3)_2\ Et_2O$ (based on analysis - 39.10 %, theoretical - 40.20 %). Further evacuation at higher temperatures led to even higher AlH_3 / Et_2O ratios.

The Preparation of Ether free Aluminium Hydride.

This method followed the previous one as far as the production of the lithium chloride free solution of aluminium hydride. Subsequent treatment was completely different,[13] instead of direct evaporation of the ethereal solution, the solution was slowly poured in a thin stream into a large volume of an inert hydrocarbon solvent (cyclohexane and isopentane were used). The effect of this was to cause the hydride to precipitate as a white fluffy solid substantially ether free. This was isolated by vacuum evaporation of the mixed solvent at room temperature.

The Attempted Preparation of t-Butyl Aluminium.

The first stage of this prepatration required the preparation of t-butyl magnesuum chloride. t-Butyl chloride in ether solution was added dropwise to magnesium under dry nitrogen. When the reaction, which was initiated by a crystal of iodine, had subsided, the mixture was refluxed for a few minutes to ensure completion and the ethereal solution of t-butyl magnesium chloride was filtered through a No.3 sinter glass filter into another flask for the subsequent reaction with aluminium trichloride.

The second stage of the reaction was carried out by adding filtered ethereal solution of aluminium trichloride to the solution of the Grignard reagent. The expected reaction was,

$$3t\text{-}Bu.MgCl + AlCl_3 \longrightarrow t\text{-}Bu\,Al + 3MgCl_2.$$

The nature of the reaction which took place was unknown since although magnesium chloride was precipitated no traces of aluminium alkyls were detected by vacuum distillation of the mixture.

Since no tri-t-butyl aluminium was prepared there was no opportunigy to look for the expected degradation to aluminium hydride. In private communication Mr. T.D.Smith states that he has prepared tri-t-butyl aluminium and that the details will be published shortly.

6. Discussion.

The various methods of preparing aluminium hydride will be described separately.

1. The Preparation of Aluminium Hydride Etherate. The methods described by H.I.Schlesinger et al. were repeated and it was confirmed than neither by removing the solvent at room temperature by evacuation, nor by allowing the

hydride to precipitate from solution, was an ether free product obtained. Some typical samples gave the following analytical results.

Sample	Aluminium Content.	Empirical Formula.
1.	43.41 %	$(AlH_3)_{2.35} \cdot Et_2O$.
2.	43.46 %	$(AlH_3)_{2.39} \cdot Et_2O$
3.	49. 03 %	$(AlH_3)_{2.90} \cdot Et_2O$.

The sample 3 was obtained after prolonged evacuation.

2. The Preparation of Ether free Aluminium Hydride.

Various means of mixing the ether solution with the inert solvent were tried but in all cases an etherated solid was formed. The content of aluminium was always between 40 and 50 % corresponding to the empirical formulae $(AlH_3)_{2.00}Et_2O$ and $(AlH_3)_{3.1}Et_2O$. The hydride obtained appeared to be ~~in~~ a more reactive form than that obtained from the direct etherate preparation. The hydride decomposed shortly after preparation, turning grey in colour and reacted vigorously with water. This is in contrast to the etherate formed by evaporation of an ethereal solution followed by high vacuum pumping where the hydride is stable on standing.

The presence of ether in the precipitated samples was confirmed by the infra-red spectra of the samples recorded in Nujol.

It is possible that, under conditions of rapid precipitation, the polymer formed is less stable than that formed by slow precipitation due to difference in the degree of polymerization achieved. It is not unlikely that a highly polymerized structure, involving a maximum number of Al...H...Al bonds, as suggested by Pitzer and Longuet-Higgins, would be the most stable form.[22]

After the publication of this section of the work, a private communication was received from Prof. T.R.P.Gibbs in which he stated that the method which he and his co-workers described for the preparation of ether free hydride, was successful in only five preparations out of a very large number of attempts. The results obtained in various industrial labotatories in the United States coincide with the findings of the present work, and he suggests that the outcome of the preparation is influenced by some unevaluated factor such as the method of preparing the ethereal solution of aluminium chloride. He further suggests that the reaction is only successful for small amounts of materials, less than two grams. He describes a proposed structure for the ether free material as an aluminium hydride polymer with lithium hydride as the terminal group and suggests that the presence of a considerable excess of aluminium would mask the presence of the lithium. This may be considered to be highly unlikely since aluminium does not interfere with the flame photometric determinations of aluminium and traces of lithium whould be easily detected.

3. The Preparation of tri-t-butyl aluminium.

The attempts at preparing this substance were wholly unsuccessful but it is probable that substances of the type $AlR_n Cl_{3-n}$ (R = t-butyl) were obtained The difficulty in preparing tri-t-butyl aluminium compared to di-t-butyl beryllium is possibly due to differences in the nature of aluminium trichloride and beryllium chloride.

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